THE HYDROGEN ION RESPONSE OF THE GLASS ELECTRODE IN ALKALINE SOLUTIONS

by

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CONTENTS

CHAPTER 1

INTRODUCTION

Soon after the demonstration of the suitability of the glass electrode for measuring pH it was found that it had the disadvantage of showing deviations from the 59mV per pH unit response in acid (pH<2) and alkaline (pH>9) solutions. Early in the development of the electrode as an analytical tool a great deal of work was carried out on the nature of these deviations. However, examination of the literature of 20 years ago reveals several discrepancies between the data obtained by different investigators, notably concerning the behaviour of electrodes made from lithia glass and the magnitudes of the errors shown by soda glass electrodes in different acid solutions.

Although the major discrepancies have now been resolved, they clearly underline the unreliability of the early work as a whole. Nevertheless one finds that certain statements which are repeatedly made in recent monographs are apparently based upon early data which have not been verified. For example, the only evidence that lithia glass electrodes show large errors in lithium hydroxide solutions dates back to 1932 and the statements that soda glass electrodes show no errors in alkaline solutions in the absence of small inorganic cations are also based upon work of this period. Furthermore some early workers presented average results whereas the data for individual electrodes showed differences possibly due to differences in their previous treatment and the extent to which they had been used.

It has now been accepted for over 15 years that lithia glass electrodes are preferable to soda glass electrodes for making pH measurements but this is based almost entirely on the fact that they show much smaller errors in sodium hydroxide solutions. However, very little data are available on their behaviour over a wide pH range and in different acid and alkaline solutions, for the principal reason that in recent years most attention has been given to the development of glass electrodes which respond to cations other than the hydrogen ion, and to the resolution of differences between the results of early investigators concerning the response of soda glass electrodes in acid solutions.

The whole question of the errors of pH responsive glass electrodes has therefore been re-examined in this department using modern electronic measuring equipment and a recently developed and proven experimental technique which enables variations in the glass electrode potential to be followed relative to a hydrogen electrode immediately after placing the glass electrode in a solution. In most previous investigations the time dependence of the glass electrode potential has not been considered and frequently glass electrode measurements have been made relative to a saturated calomel electrode with a liquid junction. In the present investigation, which is complementary to the recent work of Caudle[1,2] on the response of glass electrodes in acid solutions, the hydrogen ion response of several types of modern commercial glass electrode have been investigated over a wide pH range with a precision better than 0.01 of a

pH unit. Attention has been given to the reproducibility and time dependence of the alkaline errors, the latter feature in particular having been rarely examined in previous investigations.

In addition to the main work with pH responsive electrodes, some experiments have been carried out with electrodes primarily responsive to cations other than the hydrogen ion, since these are, in effect, electrodes which show an exaggerated alkaline error. These electrodes are usually termed simply "cation responsive" whereas those which respond primarily to the hydrogen ion, which is also a cation, are termed pH responsive electrodes. Although much work on the development of cation responsive glass electrodes has been carried out in recent years, this has taken the form of a general investigation of the dependence of the relative selectivities towards different cations in solution, including the hydrogen ion, upon tbe composition of the electrode glass. Furthermore, with the exception of a few experiments carried out in this department, the transfer technique, which has proved successful for precise measurements with pH responsive glass electrodes, has not been applied to cation responsive glass electrodes. Specimens of these electrodes have therefore been tested with this technique in order to assess the possibility of using them for precise measurements by application of the instantaneous potential idea.

The ideal experimental procedure would be direct comparison of cation responsive glass electrodes with amalgam electrodes placed in the same solutions. However, amalgam electrodes involve elaborate experimental

technique and the time dependence and reproducibility of the glass electrode potentials can be tested accurately using any reference electrode provided that the cell does not contain a liquid junction. Silver-silver chloride electrodes have therefore been employed for this purpose and, in addition, using activity coefficient data for the alkali metal chloride solutions in question, the response of the glass electrodes to changes of cation activity has been examined as a preliminary to a more rigorous investigation using amalgam electrodes. The results reported by previous investigators will be reviewed in the next two chapters, pH responsive electrodes being considered first. The experimental techniques used previously were often not entirely satisfactory and these will be discussed in the light of recent developments in chapter 5.

CHAPTER 2

Previous Investigations with pH Responsive Glass Electrodes

2.1. Selection of Electrode Glasses.

In 1928, Hughes[3] suggested criteria by which glasses for electrode fabrication might be judged, namely 1. low electrical resistance, 2. low errors and stable potentials in alkaline solutions and 3. stable asymmetry potential. Nowadays we also require low errors and stable potentials in acid solutions but in general these criteria still hold for selecting pH responsive glasses. On this basis MacInnes and Dole[4] compared a number of glass electrodes of different composition and concluded that soda lime glasses were more satisfactory than Pyrex, Jena thermometer, potassium, lithium and magnesium glasses. All the latter glasses gave unstable potentials in 0.1M NaOH solution and all but the lithium glass investigated had high resistance. Glasses containing mixtures of two alkali metal oxides were also found to have high resistances. Of the soda lime glasses, MacInnes and Dole selected the one having the composition by weight 22% Na_2O, 6% CaO and 72% SiO_2 as the best. This glass was widely used for many years and was manufactured by the Corning Glass works, New York, being designated No. 015.

In 1932, Ssokolov and Passinski[5] reported the results of an investigation which was carried out almost simultaneously with that of MacInnes and Dole and was on somewhat similar lines. They investigated the

pH response of lithium, sodium and potassium glass electrodes at 16 - 18°C in solutions of alkali metal hydroxides over a range of different concentrations. They found that their lithium glass electrodes gave the smallest deviations from the theoretical pH response; only in LiOH solutions above a pH of 11.4 were large errors observed. The error in NaOH did not appear below pH 12.5 and in KOH, RbOH and CsOH solutions the electrodes were error free below pH 13.5. These results appeared to contradict those of MacInnes and Dole. However, the differences between the findings of the two investigations, as will be seen, were probably due to the fact that glasses of somewhat different composition were used. Details of the glasses tested in both investigations are given in Table 2-1.

Gabbard and Dole[6] made further investigation of the electrode properties of the lithia glass used by Ssokolov and Passinski. They found that the electrodes had high resistances and comparatively large and unstable asymmetry potentials. Since they could not observe the correct hydrogen ion response even in the intermediate pH range (pH 2-9) they made no attempt to test the electrodes in alkaline solutions.

The question of the dependence of electrode properties upon the glass composition was much clarified by the extensive investigation of Perley[7] published in 1949. This work was carried out over 8 years and involved testing electrodes made from over 500 different glasses. He measured their electrical resistances, checked that they showed a 59mV per pH unit response in the intermediate pH range and determined the alkaline error in a solution

TABLE 2-1.

a). Glasses of MacInnes and Dole.

	Weight %			Mole %		
	Alkali Metal Oxide	CaO	SiO_2	Alkali Metal Oxide	CaO	SiO_2
1.	Li_2O 22	6	72	Li_2O 36	5	59
2.	Na_2O 22	6	72	Na_2O 21	7	72
3.	K_2O 22	6	72	K_2O 15	7	78

b). Glasses of Ssokolov and Passinski.

	Weight %				Mole %			
	Alkali Metal Oxide		CaO	SiO_2	Alkali Metal Oxide		CaO	SiO_2
1.	Li_2O	10	10	80	Li_2O	18	10	72
2.	Na_2O	20	8	72	Na_2O	19	9	72
3.	K_2O	25	10	65	K_2O	17	12	71

of pH 12.8 and a sodium concentration of 2M. Measurements were made at 25°C and buffer solutions of pH 1.0, 6.86 and 9.18 were used. No indication was given as to whether the alkaline error varied with time of immersion but the tests were repeated at intervals during the lives of the electrodes to determine whether the magnitude of the error varied with electrode age. Perley's results clearly demonstrated the superiority of electrodes made from glass containing about 25 mole % lithium oxide over those made from glasses containing the same mole % of sodium or potassium oxide. Their resistances were not appreciably higher than those of soda glass electrodes and they showed a much smaller alkaline error.

Perley also investigated the effect of varying the other components of the glass. For example, the addition of a small quantity (about 2 mole %) of lanthanum oxide was found to improve the stability of the glass and the reproducibility of the alkaline error. Also the magnitude of the alkaline error was found to be reduced by the replacement of a small quantity (about 2 mole %) of lithium oxide by caesium or rubidium oxide. On the other hand the introduction of the same amount of sodium oxide in place of lithium oxide, caused the error to increase and produced a large increase in the electrical resistance of the glass.

Although Perley confirmed the superiority of lithia glass electrodes, like Dole and Gabbard, he was unable to obtain satisfactory electrodes from glass of the composition specified by Ssokolov and Passinski, which proved unblowable and readily devitrified.[8] He also reported that he had been in

communication with the Russian workers and they had also been unable to reproduce their original results.[9] Hence it is apparent that although Ssokolov and Passinski reached the correct conclusion in 1932, that they did so was purely fortuitous.

Perley found that the most favourable lithium oxide content was 24 - 28 mole % and glasses which contained more than 28 mole % of Li_2O or less than 59 mole % of silica were unsatisfactory due to devitrification. Hence it is clear that the glass used by Ssokolov and Passinski contained insufficient lithium oxide whereas that of MacInnes and Dole contained too much. Both sets of workers reported that their lithia glass tended to devitrify and MacInnes and Dole found that the glass was also hygroscopic and electrode membranes made from it became cloudy and disintegrated after a few days in water. Perley drew attention to the importance of expressing glass compositions in mole percentages rather than weight percentages and if MacInnes and Dole had compared glasses having the same mole percentages it is possible that they would have obtained a successful lithia glass electrode. Before the publication of Perley's data, Dole[10] had suggested that the reason he and Gabbard were unable to reproduce the results of Ssokolov and Passinski might have been that their glass, prepared by the Corning Glass Works, contained some sodium oxide as an impurity. While it is now known that the presence of a small amount of sodium oxide is detrimental to the electrode properties of a lithia glass, this factor would only be of secondary importance.

Although electrode manufacturers are unwilling to disclose full details of their glass compositions, it is known that most modern commercial glass electrodes contain lithium oxide as the principal alkali metal oxide. However very little data have been published on the response characteristics of lithia glass electrodes, although presumably a number of unpublished experiments have been carried out by the manufacturers. Very little data have been available on their alkaline errors and until recently there was practically no information concerning their response in acid solutions. Perley's investigation of the alkaline errors was limited to a single sodium hydroxide solution and the errors shown by the electrodes in solutions of other hydroxides have not been examined. Hence the next section, which deals with the errors of glass electrodes, is very largely concerned with electrodes having soda glass membranes.

2.2. Errors.

The alkaline errors shown by electrodes made from Corning 015 glass at 25°C were measured by Dole[11] in 1931. He tested the electrodes in several series of solutions each with a constant cation concentration and covering a range of pH. It was found that the magnitudes of the errors increased with increasing cation concentration and depended on the nature of the cation itself, increasing in the order :-

$$Ba^{++} < K^{+} < Li^{+} < Na^{+}.$$

Subsequent investigations, such as that of Dole and Wiener[12] in 1937, showed that the alkaline errors of Corning 015 glass electrodes depended upon the temperature. They also confirmed the relative magnitudes of the errors caused by the same concentrations of different cations in solution at 25°C but some workers consistently obtained slightly larger values of the errors for given solutions than others.

These discrepancies, however, were not very large and were certainly not as serious as those between the values obtained by different workers for the acid errors, first observed by MacInnes and Belcher[13] in 1931. They found that the order of magnitude of these negative errors for different acids at the same concentration was :-

$$H_3PO_4 > H_2SO_4 > HCl.$$

and suggested that they were caused by the different anions in solution. However, in 1932 Dole[14] claimed to have found that the negative errors for

HCl and H_2SO_4 were only slightly different, in contrast to basic solutions where the positive error is much reduced if univalent sodium ions are replaced by divalent barium ions. Also addition of a quantity of neutral salt was said to have little effect upon the error unless the concentration became high. He suggested that the hydrogen ion enters the glass as H_3O^+ and that if the water activity of a solution (^aH_2O) was not unity the electrode would show an error given by

$$\Delta E = \frac{RT}{F} \ln {}^aH_2O$$

Amis and Gabbard[15] tested Corning 015 glass electrodes in solutions of up to 2M in magnesium sulphate. The solutions were buffered, either to pH 3-4 using potassium hydrogen phthalate and sodium hydroxide or to pH 7-8 using borax, and Amis and Gabbard claimed that the electrodes showed errors in agreement with Dole's equation.

Since it had been thought that some of the discrepancies in the magnitudes of the alkaline errors might have been due to the fact that the different workers had used solutions containing different anions, Dole, Roberts and Holley[16] measured the alkaline errors of Corning 015 glass electrodes in solutions containing different anions but with the same cation content. It was thought that the large errors caused by sodium solutions might mask any effects caused by the different anions and hence they used potassium solutions. They found that the magnitude of the positive error was independent of the nature of the anion in solution and concluded that the anions were without effect on the glass electrode in the alkaline pH range.

Dole, Roberts and Holley also made an interesting observation which has proved relevant to the present investigation, namely that if an electrode, which had been placed for a short period in a fluoride solution of sufficiently low pH (< about 6.5), was tested in potassium hydroxide solution an anomalously large positive error was observed. However, they were unable to obtain the same effect with sodium hydroxide solutions and suggested either that the basic action of the sodium solutions was rapid enough to dissolve off the surface corroded by the hydrofluoric acid, or that the error was already so large that the effect of the hydrofluoric acid could not be detected by the method used.

The work of Hubbard, Hamilton and Finn[17] tended to confirm the view that the acid errors were due to the different anions in solution rather than a lowering of the water activity; but in contrast to MacInnes and Belcher, they found that their Corning 015 glass electrodes gave much larger errors in HCl than in H_2SO_4 where there was no error up to 10N. They also made measurements with Corning 015 glass electrodes in hydrofluoric acid solutions up to 1N and observed large errors (>>HCl) even in dilute solutions. Furthermore electrodes made from a commercial glass (designated "glass A") having composition (presumably by weight)

13.5% Na_2O : 10.1% CaO : 3.3% MgO : 0.7% R_2O_3 : 72.1% SiO_2

gave very much smaller errors than the Corning 015 glass electrodes in HCl solutions whereas Dole's water activity theory implies that the magnitude of the acid errors should be independent of glass composition.

The contradictory nature of the early literature concerning the acid errors of soda glass electrodes, together with the alternative theories that were put forward, aroused considerable controversy. Consequently in subsequent years, the errors of these electrodes in acid solutions received much more attention than the alkaline errors and the investigations that have been carried out in order to resolve the discrepancies contained in the early data, will now be reviewed.

Testing the glass electrode over a wide pH range Izmailov and Alexandrova[18] have found that the calibration curve for electrodes made from Hughes' glass :-

Wt%			Mole %		
Na_2O	CaO	SiO_2	Na_2O	CaO	SiO_2
20	8	72	19	8	72

passes through a minimum in strongly acid solutions. The calibration curve for MacInnes - Dole glass electrodes also was found to show deviations from linearity in the acid region but no minimum was observed. They subsequently found that for Hughes' glass electrodes, the pH at which the errors appear and the position of the minimum of the curve depend upon the nature of the acid, the errors being larger in HCl than in H_2SO_4. Izmailov and Alexandrova also claimed that in strong acid solutions the glass electrode behaves as a reversible anion electrode. This conclusion was reached on the basis of a series of experiments with solutions containing salts and high concentrations of the corresponding acid, when the potential of the glass electrode was said to show a linear dependence on the logarithm of the anion activity.

Sinclair and Martell[19] drew attention to the fact that the magnitudes of the acid errors depend upon the time of immersion. For all the different types of glass which they examined, the response in strongly acid solutions was distinctly different to that in dilute solutions. They observed that the glass-hydrogen electrode e.m.f. "rapidly attains a steady and reproducible value in both HCl and H_2SO_4 solutions of concentrations of about 1N and less but that the attainment of a steady e.m.f. value in solutions more concentrated than 1N is a much slower process." Most of the e.m.f. values which they quoted for more concentrated acid solutions were,so they pointed out, not necessarily constant values but were those recorded, after three hours observation. In a few cases the e.m.f. variation was followed over a period of 15 hours. For a number of electrodes investigated, including those made of Corning 015 glass, the observed acid errors did not agree with those predicted by Dole's equation and whereas the large errors observed in HCl solutions might be due to attack of the glass, Dole's theory cannot explain the errors in H_2SO_4 solutions which are much smaller than predicted by the equation.

In the work of Glöckner,[20] and Schwabe and Glöckner,[21] electrodes of MacInnes-Dole soda glass were tested in phosphoric, sulphuric and hydrochloric acids and the potentials were followed for up to 30 hours or more. Their results confirm the general observations of Sinclair and Martell for HCl and H_2SO_4 and show that the errors in H_3PO_4, which are lower than for sulphuric acid, are also lower than the values predicted by Dole's equation. They also

found that the potential fall observed in strong acids is steeper and of longer duration the more concentrated the solution and the higher the temperature. Schwabe and Glöckner suggested that the errors of soda glass electrodes in acid solutions are due to the absorption of excess hydrogen ions together with the corresponding quantity of anion possibly as undissociated molecules.

The work of Schwabe and Glöckner has been extended by Boksay, Csákvári and Lengyel.[22] These workers tested electrodes made from a lithia glass in up to 9N HCl and in 4 and 5.8N $HClO_4$ solutions. For the concentrated HCl solutions the glass electrode potentials showed a time dependence whereas for the perchloric acid they were constant within the precision of the experimental method (± 0.5mV) for several hours.

In order to determine whether anions do in fact enter a glass electrode surface from concentrated acid solutions, radioactive tracer techniques have been applied by two groups of workers. Schwabe, Dahms, Nguyen and Hoffmann[23] used MacInnes - Dole glass electrodes and investigated the effect of 4m solutions of HCl, HBr and HI and 10m solutions of H_2SO_4 and H_3PO_4. The uptake of anions in the halogen acids corresponded to the relative magnitudes and time dependence of the observed errors, but although their electrodes gave errors in sulphuric and phosphoric acids they were unable to detect any radioactivity in the glass even after 20 hours immersion in these latter solutions. The other investigation was that of Izmailov and Vasilev,[24] who used radioactive isotopes of bromine, sulphur, calcium and sodium with Hughes'

glass, in the form of both electrodes and plates. They found that adsorption of anions depended upon the acidity of the solution, the concentration of the adsorbing ions, the time of immersion and the time of washing. There was little or no cation adsorption in acid solutions. The adsorption of sulphate and bromide ions in alkaline, neutral or weakly acid solutions was almost absent but on increasing the acidity, the adsorption of anions increased sharply at points corresponding to the appearance of the respective acid errors. The increase in adsorption with time of immersion corresponded to the observed time dependence of the acid error.

In addition to these experiments with acid solutions, both Schwabe[25] and Izmailov,[26] and their collaborators, have used radioactive tracers to investigate whether the alkaline errors of glass electrodes are also associated with the adsorption of ions. These investigations have been carried out mainly with soda glasses because soda glass electrodes show large alkaline errors and hence if the errors are due to adsorption of ions large effects should be observed. However, Schwabe and Dahms[25] have also carried out a few experiments with a lithia glass. Both investigations used radioactive isotopes of sodium, potassium, caesium and bromine and generally concordant results were obtained. It was found that the cations were adsorbed by the glass electrodes in amounts which increased with increasing cation concentration, pH of the solution and time of immersion. No adsorption of bromide ions was observed and hence the cations were not adsorbed as neutral salt. At high pH it was observed that a degree of saturation was

reached and the amount of adsorbed ion either became constant or even decreased as the pH was raised. It was suggested that this decrease in adsorption was due to the increased solubility of the glass in alkaline solutions.

The results of both investigations show a clear correlation between the adsorption of cations and the alkaline errors of soda glass electrodes. For example, for sodium solutions in the intermediate pH range, (about 1-8.5) where the glass electrodes show no error, no large amounts of adsorption were observed but a marked increase in the adsorption was found to occur at about pH 8.5, the point at which the electrodes begin to show deviations. Also, the relative amounts of adsorption of the different cations, under similar conditions of pH, cation concentration and time of contact with the solution, were found to be in the order $Na^+ > K^+ > Cs^+$ which corresponds to the relative magnitudes of the alkaline errors for solutions containing these cations. Further evidence for this correlation is shown by the data of Schwabe and Dahms for their lithia glass electrodes. These did not show adsorption of sodium ions until above pH 12 and this corresponds to the point at which they begin to show appreciable errors in sodium solutions.

If, as suggested by the results of these experiments with radioactive tracers, the alkaline errors of glass electrodes are due to penetration of the glass surface by small inorganic cations, no errors should be observed in alkaline solutions from which these small ions are absent. A few experiments have been carried out by previous workers using alkaline solutions

having only large organic cations and also with ammonia buffers. MacInnes, Dole[4,13,16] and their collaborators found that their soda glass electrodes gave much smaller errors in solutions of guanidine or the tetra-alkyl-ammonium hydroxides than in hydroxides of the alkali metals. In 1929, Hill[27] tested soda glass electrodes in ammonia buffers of pH up to 11.4 with and without added sodium chloride. He found that "considering the experimental error of the method, 0.01 pH" the electrodes showed no errors in the absence of added salt but in buffers containing 0.5M NaCl, errors were observed above pH 8.6. Hubbard, Hamilton and Finn[17] also observed that soda glass electrodes showed no errors in ammonia solutions.

It was noted earlier that very little work has been carried out with the modern lithia glass electrodes. However, Simon and his co-workers[72,73] have investigated the response characteristics of a number of electrodes which they themselves made from samples of various commercially available glasses supplied to them by the manufacturers. These glasses included those used for certain types of commercial electrode tested in the present work and hence their results will be described in some detail. Using tartrate, phosphate and borax buffers, they checked that the hydrogen ion response of their electrodes in the intermediate pH range was of the order of 59mV. per pH unit, although as will be seen their experimental procedure did not permit very high accuracy. They also investigated the magnitudes of the alkaline errors in 0.1M and 1.0M sodium hydroxide solutions and their data confirmed that electrodes made from lithia glasses show smaller errors in alkaline solutions than do soda glass electrodes.

They found that the magnitude of the error depended upon the time of immersion, particularly for the more concentrated solution, and this made it difficult to specify a definite alkaline error. However they quote the first observed error (3-10 minutes after contact with the solution) for both solutions and in the case of the 1.0M solution the potential variation for each electrode was observed over two hours and qualitatively designated to one of the following types:

A. Potential continuously increased

B. Potential continuously decreased

C. Potential increased until a more or less constant value was attained

D. Potential decreased until a more or less constant value was attained

E. Potential initially decreased but then began increasing

F. Potential initially increased but then began decreasing.

Simon and his collaborators found that an e.m.f.-time variation could not always be unambiguously assigned to one particular type. Also two types of e.m.f.-time variation were sometimes observed in different experiments with electrodes having the same glass. They therefore found it necessary to use a double symbol in these cases. In the discussion, the e.m.f.-time variations reported by Simon and his collaborators will be compared with those observed in the present work for electrodes having the same glasses.

2.3. Recent Considerations.

In the light of the observations of the time dependence of the magnitude of the glass electrode errors in strong acid solutions, Beck and Wynne-Jones[28] suggested that "two potentials have to be distinguished.

1) The potential instantaneously set up at the glass surface in each solution. This potential varies only with the activity of the hydrogen ion in the solution and in quantitatively the same manner as for a hydrogen electrode.

2) An asymmetry potential which changes with time and is caused by exchange of ions or water with the solution. Consequently if there is an exchange of water, the electrode potential may appear to vary with the water activity but as it is doubtful if true equilibrium is reached when there are large variations in the water activity the actual value of the potential will depend upon the time of measurement. On the other hand, if ions are exchanged, the electrode potential will show a dependence upon the concentration of those ions in the solution and the electrode may appear to behave reversibly to ions other than the hydrogen ion, but this potential will also vary with time."

Up to that time, investigations of the acid errors of glass electrodes had not included measurements of the electrode potential at times soon after transfer to a strong acid solution. For example, Sinclair and Martell[19] took their first reading in 5M HCl about half an hour after the electrode

was placed in the solution and then took further readings over a period of 15 hours. Beck and Wynne-Jones considered that the data suggested that a large change of potential might occur during the first half hour and that if this could be traced back, the error at the instant of transfer would be zero. They also commented on the conflicting reports concerning the reproducibility of the alkaline errors and pointed out that it was not clear from the literature whether due attention had been given to asymmetry potential changes. They suggested that the potential of a glass electrode in alkaline solutions might be time dependent and on the basis of the ion exchange theory put forward by Nicolsky,[29] they proposed that the alkaline errors might also be asymmetry potential changes. According to this theory the alkaline errors are due to exchange of the H^+ ions in the glass for metal ions in the solution resulting in a change of the chemical potential of the hydrogen ions in the glass and so a deviation from the hydrogen electrode function. If this exchange takes place slowly then the instantaneous potential of the glass electrode in an alkaline solution immediately after transfer from a solution of intermediate pH should show zero error, since no exchange has taken place and the surface of the glass is in the same condition as in the previous solution.

Covington and Prue[30] showed how the hypothesis of Beck and Wynne-Jones could be applied to obtain quantitative data, accurate to better than 0.1mV, with soda glass electrodes in dilute acid solutions. They transferred a low resistance glass electrode, washing it with the new solution, between

the following cells

Ag-AgCl	HCl (m_1)	Glass	HCl (m)	Ag-AgCl	(A)
Ag-AgCl	HCl (m_2)	Glass	HCl (m)	Ag-AgCl	(B)

and by an extrapolation procedure obtained the e.m.f's. of the two cells at the moment of transfer. At this instant the asymmetry potential makes the same contribution to the e.m.f's. of both cells and they observed the e.m.f. difference to be in agreement with that which would be obtained if two hydrogen electrodes were placed in the same cells.

Caudle[1] applied the technique of Covington and Prue to an investigation of the suggestion made by Beck and Wynne-Jones, that the errors observed in strong acid solutions were merely changes of asymmetry potential. Various commercial glass electrodes were tested by transferring them between cells containing acid solutions of various concentrations and hydrogen electrodes. If a glass electrode behaved as a hydrogen electrode the e.m.f. of a pair of cells would be identical at the instant of transferring the glass electrode between them, and any subsequent time variation of the e.m.f. could be regarded as a change of asymmetry potential. When this was not so, any time variation could be described as a time dependent error being the difference between the e.m.f. at a certain time in the second solution and the final e.m.f. in the first solution.

It was found that the e.m.f.-time variations might contain the following features either singly or combined:

(A) a rapid change over the first few minutes which was largely independent of solution composition and concentration and was probably electrical rather than electrochemical in origin;

(B) a zero, or slight and approximately linear, change; and

(C) a rapid change, the rate of which slowly decreased, but a steady value rarely being reached even after many hours.

The electrodes tested could be broadly divided into two groups according to their behaviour. Soda glass electrodes, for which (A) was absent, gave (B) at low and intermediate acid concentrations and extrapolation to the instant of transfer showed no error ($\pm$ 0.1mV). Above a molality dependent upon the acid anion HCl (1m), HBr (5m), H_2SO_4 (7m); H_3PO_4, CH_3COOH and $HClO_4$ (10m) characteristic behaviour (C) was found. The error became more negative with time and increasing acid concentration. Reasonable extrapolation of the non-linear e.m.f.-time curve gave smaller but apparently non-zero errors. "General purpose" electrodes, believed to be made from lithia glass, gave e.m.f.-time curves consisting of features (A) and (B), the linear portion when extrapolated to the time of transfer possibly indicating an error of $\pm$ 0.3mV; only at very high acid concentrations were (A) and (C) observed.

Zielen,[31] using Beckman General Purpose electrodes, also demonstrated the validity of the transfer technique (if by a rather elaborate method) for making precise measurements with the glass electrode. He tested these lithia glass electrodes in various strong acid solutions and in most cases

observed agreement with hydrogen electrodes to better than 0.05mV at the instant of transfer between 2 cells. Only in HCl more concentrated than 1 molar were errors observed. These amounted to no more than 3mV. in a 4m solution.

The investigations of Caudle and Zielen indicate that genuine acid errors of the glass electrode do exist though Zielen suggests that "ideal behaviour appears to be more the norm than the exception." In the present work the principles and experimental techniques of Caudle have been applied to a reinvestigation of the alkaline errors of glass electrodes. It was proposed first of all to confirm that the alkaline errors observed by previous workers, like the acid errors, were real and not simply changes of asymmetry potential as suggested by Beck and Wynne-Jones. Particular attention has been paid to the time dependence of the errors as well as the relative magnitudes of the errors shown in solutions containing different cations.

Although it has been shown that the errors of glass electrodes cannot in general be regarded as changes of asymmetry potential, the hypothesis of Beck and Wynne-Jones has nevertheless provided the basis of the method developed for making precise pH measurements with the glass electrode in solutions where errors are not observed. However, until now, the validity of this transfer technique has only been proven for acid solutions and a further purpose of this work was to investigate whether it could be applied over a much wider pH range. Also in this work, the testing has been extended to include a larger number of different types of commercial glass electrode.

CHAPTER 3.

Previous Investigations with Cation Responsive Glass Electrodes

3.1. Development.

The previous work on cation responsive glass electrodes will be reviewed in this chapter in so far as it is relevant to the present investigation. Although much attention has been given to the dependence of electrode properties on glass composition, this work will only be outlined briefly, since it has not been possible to investigate this aspect here as only commercial electrodes have been employed. This review will in general also be limited to experiments with aqueous solutions containing only one cation in addition to the hydrogen ion, since solutions containing other mixtures of cations were not used in the present work.

Early in the development of the glass electrode, Horovitz[32] and Schiller[33] noticed that addition of small amounts of aluminium or boric oxides to a pH responsive glass caused enhancement of the alkaline error and Hughes[34] found that the less Al_2O_3 a glass contained the better was its pH response. In 1934, Lengyel and Blum[35] conclusively demonstrated that the presence of Al_2O_3 or B_2O_3, or both, in a glass resulted in its electrode response becoming strongly dependent upon the sodium concentration of the solution. They investigated the electrode properties of a number of glasses of different composition, in sodium solutions of different pH, and found that the glasses could be divided into two groups independently of their basic

oxide content :-

a). Glasses similar to that of MacInnes and Dole which showed a pH response up to the onset of the alkaline errors at pH 8 - 9

b). those in which some of the SiO_2 had been replaced by the other acidic oxides, Al_2O_3 and B_2O_3. These produced electrodes whose potentials were independent of pH and dependent upon the sodium concentration above a pH of about 4. Below this pH they showed a mixed electrode function, becoming completely hydrogen ion responsive in strong acid solutions.

The work of Lengyel and Blum has been considerably extended by Eisenman[36,37] and by the Russians: Nikolsky, Shultz and their collaborators.[38] However, these investigations have, in general, also been concerned with the effects of variations of glass composition on the essential features of the electrode response. Consequently a large number of electrodes of the different glass compositions were tested at comparatively low level precision.

Apparently working independently, these two sets of investigators showed that the introduction of Al_2O_3 not only produced a response to sodium ions but also resulted in a reproducible response to other alkali metal cations. Eisenman, Rudin and Casby,[36] for example, paid particular attention to the relative sensitivities to different cations shown by their electrode glasses. The relative sensitivity or selectivity may be regarded as a measure of the extent to which an electrode shows the theoretical response to one ion in the presence of another. They found that all glasses containing Al_2O_3 were markedly cation sensitive relative to the hydrogen ion and the

relative sensitivity for the different cations was a systematic and reproducible function of glass composition. Both sets of investigators observed the importance of aluminium to sodium ratio in determining the selectivities shown by the various sodium alumino-silicate glasses to different alkali metal cations. For example, as the ratio is increased the glass shows a greater selectivity for sodium relative to potassium. They also found that cation sensitive electrodes can be obtained from glasses in which the Al_2O_3 or B_2O_3 is replaced by the oxide of certain other trivalent elements such as gallium or scandium. They therefore compared the electrode properties of glass systems containing different combinations of the various alkali metal and trivalent ions. Eisenman[37] concluded that there exists a pattern of selectivities shown by all the glass systems which he had investigated and suggested that this pattern constitutes a quantitative "Glass Specificity Rule". He pointed out that the existence of this rule reduces substantially the number of experiments necessary to characterise an electrode glass. A measurement of Na-K selectivity (with at most an additional measurement of Cs-K selectivity) will usually suffice to permit prediction of the sequence of selectivities for the other alkali metal ions and also for the alkaline earth, silver, thallous and ammonium ions. This relationship between the various selectivities contributed to Eisenman's success in finding the glasses most responsive to various different cations and some of these had sufficiently high selectivities to be of practical use.

Besides investigating the relative selectivities of the various glasses for different cations Eisenman, Rudin and Casby examined the time dependence, stability and reproducibility of the electrode potential. They concluded that their potassium selective glass "responds in a 'square' manner to step changes of solution composition in mixtures of the hydrogen ion and the alkali metal cations," whereas their sodium selective glass exhibits transients in some solutions. An approximately steady state was found to be achieved after 500 seconds (i.e. < 10 mins.) Eisenman[39] also measured activity coefficients of sodium chloride solutions using electrodes made from the glass which he found to have the best sodium response. This work will be considered later together with other similar investigations.

With the co-operation of Eisenman, Mattock[40] has succeeded in producing an electrode glass which is not only more easily workable but more sodium selective than the one which Eisenman had originally recommended. Until recently, this glass, known as BH 68, has been commercially available for laboratory use from Electronic Instruments Limited as the GNA 33 electrode and one electrode of this type, obtained before their withdrawal from the market, has been tested in this work. Mattock later developed a second sodium selective glass known as BH104, which is said to be a little faster in response and capable of providing highly reproducible results particularly with relatively concentrated sodium solutions. Subsequently[41] he also developed an electrode glass which was responsive to potassium and ammonium ions. This glass, number BH115, and also the sodium responsive BH104 glass

are at present available from Electronic Instruments Limited in the form of the GKN 33 and GEA 33 electrodes respectively. Since the present work has been carried out with electrodes of these two types together with the GNA 33 electrode referred to above, the findings of Mattock will now be discussed in more detail.

Mattock's experimental technique was apparently determined by the fact that cation responsive glass electrodes are often used to determine cation concentrations rather than activities and in these circumstances it is convenient, if possible, to keep the cation activity coefficient constant. For example, in the case of a glass electrode which only responds to sodium ions the e.m.f. of the cell:

$$\text{glass} \;\Big|\; Na^{+} \;\Big|\; \text{Sat. KCl} \;\Big|\; Hg_2Cl_2 - Hg$$

will be given by:

$$E = E' - 2.303 \frac{RT}{F} \log a_{Na^+}$$

where a_{Na^+} is the activity of sodium ions and E' is a constant in so far as the asymmetry potential of the glass electrode and the liquid junction potential are constant. If the sodium ion activity coefficient is kept constant the e.m.f. becomes proportional to $-\log c_{Na^+}$, where c_{Na^+} is the sodium ion concentration, since the above equation can now be written:

$$E = E'' - 2.303 \frac{RT}{F} \log c_{Na^+}$$

E", like E', is approximately constant. Mattock therefore tested electrodes made from the above mentioned glasses, in buffer solutions, which not only provided a constant known pH but were of a sufficiently high concentration

to maintain constant ionic strength when the concentration of sodium or potassium ions was varied. Ethanolamine and triethanolamine with HCl or HNO_3 were suitable for this purpose and in this way the sodium or potassium ion activity coefficient was kept approximately constant in all but the strongest solutions employed. This procedure is recommended by Electronic Instruments Limited[42-45] when it is desired to measure sodium or potassium concentrations rather than activities. In a case where the use of buffers is undesirable they suggest as an alternative that a calibration curve for the empirical scale pNa = -log $c_{Na}+$ should be set up using solutions of similar anion and cation content and ionic strength to those under investigation.

From the sodium responsive BH68 and BH104 glasses, Mattock prepared bulb type electrodes with resistances of about 50 megohms at room temperature. The inner reference system was either 0.1M hydrochloric acid or hydrochloric acid-sodium acetate mixture with a silver-silver chloride electrode and both were equally satisfactory. E.m.f. measurements were made relative to a saturated calomel electrode with or without a secondary salt bridge of the buffer medium used in the test solution. The electrodes were tested in several series of solutions covering the sodium concentration range 1 to 10^{-5} M at various different pH values. At a pH of 7 or above they showed a linear response to change in pNa over the pNa range 1-4 but the response was only 90-95% of the theoretical. It was suggested that the background medium might exert some influence and there may have been some variation in the sodium ion activity coefficient particularly at the higher concentrations.

A reproducibility of between ± 0.01 and 0.02 of a pNa unit was observed for the 0-3 pNa range. The response time, defined as the time taken to reach a steady reading within stated limits, was said to be generally longer with sodium responsive electrodes than with pH electrodes.

Mattock also investigated the influence of other cations present in the solution upon the sodium response, and particular attention was given to the errors caused by the hydrogen ion at low pH. It was found that electrodes made from the BH68 glass showed smaller errors than those made from BH104 and hence the former had a higher selectivity towards the sodium ion. No indication of the time dependence of these errors was given. Of the other cations investigated lithium had the largest influence. In fact the possibility of using BH68 glass electrodes as responsive to lithium, silver or thallous ions was subsequently examined[46] and of these, the first two appeared promising. The silver response in particular might be worthy of further investigation.

The testing procedure for the BH115 electrode[41] was in most respects the same as that previously used for the BH68 and BH104 sodium responsive electrodes. Bulb type electrodes with resistances of about 40 megohms were used and the inner reference system was a phosphate buffer with added potassium chloride and a silver-silver chloride electrode. A calomel reference electrode with 3.6M potassium chloride was used but in this case it was found that the use of an intermediate bridge was essential to prevent potassium chloride from leaking into the test solution. The buffer medium

used for the test solutions was found to be most convenient for this purpose and it was necessary to renew this for each daily series of measurements.

The electrodes showed a linear response to ammonium or potassium ions which was 90-95% of the theoretical value over the concentration range 0.5 to 0.001M (i.e. up to a pK of 3) and the reproducibility was ± 0.01 pK unit. From the graphical presentation of the data it appears that pH has less effect upon these electrodes than on the two types of sodium responsive electrode investigated. Mattock recommended that for electrodes made from BH115 glass, potassium solutions having a pH of not less than 6 should be used, and above this pH the speed of response was said to be comparable with that of pH responsive glass electrodes.

Savage and Isard[47-49] investigated the cation response of various electrode glasses, mostly sodium aluminosilicates and borosilicates and paid particular attention to the time variation of the potentials since Eisenman had only been concerned with the steady values.[49] Their electrodes were tested in solutions of NaCl, KCl and Li_2SO_4 of concentrations 1 to 10^{-4} N buffered at pH 7.80 ± 0.05 with triethanolamine and HCl. They were conditioned for at least one day in 0.01N NaCl before the experiments with NaCl solutions and similar treatment was given in 0.01N KCl and 0.01N Li_2SO_4 before testing in solutions of these salts. The glass electrodes were filled with 0.1N HCl and a silver-silver chloride electrode was used as internal reference. Potentials were measured relative to saturated calomel reference electrodes but these were not at the same temperature as the

glass electrodes![49] In general the electrodes showed a slow response to changes in cation concentration and required times from a few minutes up to an hour to achieve a steady potential. The changes of potential varied from a few millivolts up to 20mV. or more and their direction depended on the order of testing in the different solutions. They investigated the possibility that the variations of e.m.f. were due to diffusion of potassium ions from the saturated potassium chloride into the region of the glass electrodes but concluded that interference from this source was small and could not account for the large variations observed. However, the arrangement of Mattock with a bridge solution separating the test solution and the potassium chloride is undoubtedly preferable if a saturated calomel electrode is to be used in experiments with cation responsive electrodes.

3.2. Measurement of Activity Coefficients with Cation Responsive Glass Electrodes.

A few attempts have been made to determine whether cation responsive glass electrodes might be used to measure activities and activity coefficients of electrolytes but these have been almost entirely limited to sodium chloride solutions using cells with silver-silver chloride electrodes. The e.m.f. difference for a pair of such cells corresponds to the concentration cell

$$\text{Ag-AgCl} \;\Big|\; \text{NaCl}\ (m_1) \;\Big|\; \begin{matrix}\text{glass} \\ \text{electrode}\end{matrix} \;-\; \begin{matrix}\text{glass} \\ \text{electrode}\end{matrix} \;\Big|\; \text{NaCl}\ (m_2) \;\Big|\; \text{AgCl-Ag}$$

and there are three possible ways of examining whether the glass electrode shows the theoretical response to sodium ion activity.

1. A reference concentration may be selected and using a literature value of the activity coefficient of NaCl in this solution, the activity coefficients for the other concentrations may be calculated from the glass electrode e.m.f's. These are then compared with the published values.

2. Literature values of activity coefficients may be used to calculate the theoretical e.m.f's. and the values obtained with the glass electrode are then compared with these.

3. One solution of the concentration cell is kept constant while the other is varied. Activity coefficient values are then obtained from the e.m.f. data, using a graphical extrapolation to infinite dilution, and are compared with the literature data.

The first procedure has been used by Eisenman whereas the second has been

employed by Covington[50] and by Lanier[51] and also in the present work. The third procedure was used in the recent work of Hostetler, Truesdell and Christ[52] with potassium chloride solutions.

Lanier[51] working with Beckman glass electrodes, measured the e.m.f. differences of pairs of cells of the type

glass | NaCl (m) | AgCl-Ag

at 25°C and compared the values with those predicted using activity coefficient data from three different sources:

a). that of Harned and Nims[53] obtained using sodium amalgam electrodes

b). that obtained from isopiestic measurements by Scatchard[54] et al.

c). that listed by Robinson and Stokes.[55]

First of all he investigated the effect of change of pH upon the glass electrodes by measuring the change of potential of the electrode for change in pH of 3 to 12 in 0.1m NaCl and concluded that the response was 0.05mV per pH unit above pH5. Presumably a series of buffered solutions were used for this test but it is not clear whether variations of the sodium chloride activity coefficient in these solutions were taken into account.

When making measurements with the unbuffered sodium chloride solutions the instantaneous potential idea was apparently not applied since "readings were recorded when the drift of potential became negligible." Nevertheless the precision obtained was ± 0.2mV. Lanier found that comparison with the literature data was difficult since the e.m.f. values predicted by the different sources disagreed with each other by as much as 1mV for concentrations

above 1.5m. However the results obtained with the glass electrode agreed with the literature about as well as the literature values agreed with each other.

Eisenman[39] used glass electrodes to measure activity coefficients of NaCl solutions over the concentration range 0.1 to 6m. His experimental technique was essentially the same as that of Lanier but he used 'flow through' electrodes made from the glass which he had found most suitable for sodium solutions. Measurements were made at 0, 25 and 50°C and three separate experimental runs were carried out at each temperature.

The activity coefficient data obtained at 25°C were compared with the values of Robinson and Stokes[55] taking the 1m. solution as a reference point. Activity coefficient values for the other concentrations were thus calculated from the data for each experimental run using the value given by Robinson and Stokes for the 1m. solution. The activity coefficients obtained from the separate experimental runs sometimes differed by 1% - corresponding to differences of 1mV in the e.m.f. of the above concentration cell - and showed only approximate agreement with the values of Robinson and Stokes. The experimental data for the other two temperatures was compared with the activity coefficient values given by Harned and Owen[56] and showed a similar level of precision. Eisenman also measured activity coefficients of LiCl solutions using a glass electrode. However the agreement between the experimental data and the literature values (source not stated) was even less satisfactory than that for the NaCl solutions.

Covington[50] tested a GNA 33 electrode in NaCl solutions of molalities 0.001 to 1 at 25°C. The electrode was transferred between cells containing pre-equilibrated silver-silver chloride reference electrodes, each time washing it with a sample of the new solution at the same temperature. The pH of the solutions was measured with an E.I.L. GG 33 electrode and found to be 4.4. The electrode responded to changes in sodium concentration more slowly than stated by Mattock[40] and the manufacturer,[42] taking up to three hours, depending upon the concentration change, to reach a steady value. Theoretical values of the e.m.f. differences for pairs of cells were calculated from activity coefficients, γ , obtained (for molalities up to 0.1m) from the equation[57]

$$\log \gamma = \frac{-0.5084\ m^{\frac{1}{2}}}{1 + m^{\frac{1}{2}}} + 0.13m$$

and for 1m using 0.657, the value given by Robinson and Stokes. The calculated e.m.f. differences were compared with the differences between the steady final e.m.f's. shown by the cells with the glass electrode since extrapolation to the instant of transfer was not possible. The electrode was found to give an approximately theoretical response to changes of sodium ion activity, the mean error being 0.035 pNa unit.

Hostetler, Truesdell and Christ used a Beckman potassium selective glass electrode to determine activity coefficients of aqueous potassium chloride solutions over a range of temperatures including 25°C. They made e.m.f. measurements for pairs of cells

glass electrode | KCl (m) | AgCl-Ag

and although they apparently recognised that the asymmetry potential of a glass electrode varies with time, they considered that it could be taken as constant between successive e.m.f. measurements with solutions of relatively small differences in concentration. However they gave no indication of the reproducibility of the e.m.f. differences for the various pairs of cells.

3.3 Summary.

In the present investigation experiments have been carried out using commercial cation responsive electrodes supplied by E.I.L. similar to those tested by Mattock.[40,41] Mattock's experiments established the general usefulness of the electrodes and the present work has been concerned with examining their suitability for more precise measurements. The electrodes have been tested using the transfer technique, which has proved successful in revealing the fast response of pH sensitive glass electrodes, and the time dependence of the potentials has been followed using cells without liquid junction whereas Mattock used saturated calomel reference electrodes. Although Mattock investigated the magnitude of the errors caused by the hydrogen ion at low pH, he did not report any details of their time dependence and this has therefore also been investigated. In addition the response of the electrodes to changes of cation activity has been examined since Mattock's work was only concerned with changes of cation concentration and it was reported that the response was only about 95% of the theoretical. On the other hand, this work has been limited to solutions of a single metal cation - namely the one for which the respective electrodes are primarily intended - and different pH. Interference by other metal ions has not been investigated.

Discrepancies exist between the data of previous investigations, concerning the speed of response of cation sensitive glass electrodes.

Mattock[40,41] reported response times of the order of a few minutes and this was apparently confirmed by Eisenman's work.[36] On the other hand Covington,[50] and Savage and Isard[47,48] observed much longer times. This will be discussed in more detail later since the results of the present work suggest possible reasons for these differences.

CHAPTER 4

Experimental Equipment and Materials

4.1. Equipment.

Thermostat: The transfer experiments were carried out in an air thermostat which consisted of a wooden cabinet at bench height, itself about three feet high, insulated with 2" cork slabs and expanded polystyrene sheeting. The interior was covered with aluminium sheeting mounted so as to ensure efficient circulation of the air by an electrically driven fan and maintained at earthed potential to provide shielding for the cells. The air temperature which was checked by two thermometers, one in air and one in water, was controlled to 25 ± 0.1°C. by electrical heaters and a large mercury-toluene regulator mounted on the back wall. The door of the thermostat contained a double glazed window and two arm holes by means of which glass electrode transfers could be made without causing significant change in the air temperature. These holes were covered when not in use although the temperature appeared to be unchanged when they were left open.

Measuring Circuit: The glass-hydrogen electrode e.m.f. was measured with a Tinsley potentiometer, type 4025, and an E.I.L. - Harwell type 1086A vibrating condenser electrometer. The current output from the electrometer was passed through a suitable resistance and the resultant potential was measured by a 10mV Honeywell-Brown recorder. The potentiometer was connected

in series with the cell across the electrometer input and supplied a potential in opposition to the cell e.m.f. The potential difference, which was arranged to be less than 10mV, was measured by the electrometer and small changes in the e.m.f. could be continuously followed on the recorder with an accuracy of 0.1mV. Hence the stability of the measuring circuit was of utmost importance and in the electrometer this was achieved to a large extent by negative feedback. The recorder incorporated an automatic standardising circuit but nevertheless calibration checks were carried out on the electrometer-recorder combination by means of a potential from the standardised potentiometer. The lead accumulator was always connected to the potentiometer at least twelve hours before use so that it was supplying a steady current during the period of making measurements. During an experimental run, the whole circuit was standardised at intervals of approximately two hours; the drift was usually slight and never more than 0.1mV. The Weston standard cell used for calibration was checked against an N.P.L. standard within the department and the galvanometer terminals were short circuited after standardisation to guard the galvanometer during the experimental runs.

A ceramic switch with an insulation resistance of $> 10^{12}$ ohms when dry served as an external 'set zero' switch for the electrometer. A similar switch acted as a glass electrode selector switch and both were mounted in a sealed metal box containing silica gel. This was placed inside the air thermostat to reduce to a minimum the time required to switch on the measuring circuit after a glass electrode transfer. The connections from the

switch box to the electrometer were made with Telcon non-microphonic cable Type PT I GM (MOD) and Belling Lee B.S. television plugs and sockets. The screening of the coaxial leads and the metal case of the switch box were at earth potential.

It was important that the response of the measuring circuit should be rapid, and the speed of response of the whole circuit, including the pen recorder, could be observed either by making a sudden variation of the potentiometer setting during a measurement, or by switching from 'set zero' to measure the e.m.f. of a glass electrode cell, some time after first placing the glass electrode in the solution. No lag was detected, the first e.m.f. reading being observed on the recorder in about 2-3 seconds.

Transfer Cell: It is a requirement of the transfer technique of Covington and Prue that the reference electrodes in the different cells should have previously attained thermal and electrochemical equilibrium and should not be disturbed by the transfer process. This necessitates certain experimental precautions particularly if the hydrogen electrode is to be used. If the hydrogen and glass electrodes are contained in the same cell compartment, then unless the glass electrode is washed with solution saturated with hydrogen the hydrogen electrode will be disturbed. On the other hand if the glass and hydrogen electrodes have separate compartments, then since the hydrogen electrode compartment must have an opening for the escape of gas, mechanical movement of the solution might occur when the

glass electrode is placed in the cell, and this could cause solution not saturated with hydrogen to move into the vicinity of the hydrogen electrode. This difficulty was overcome by Caudle who designed a cell of the type used in this investigation. It was made of pyrex glass and consisted of three electrode compartments arranged in a line and separated by 4mm. taps. The centre compartment, which incorporated a B45 socket, was designed for the glass electrode and the other compartments with B19 sockets were suitable for two hydrogen electrodes. However in the present series of experiments only one hydrogen electrode was used in each cell and the other compartment contained a reference electrode reversible to an anion. The cell was therefore essentially as shown in figure 1. Both taps of the cell were lightly greased with Apiezon non-silicone grease (type L) around the top and bottom so that annular rings of solution could form within them thereby giving electrical contact in the closed position. If the e.m.f.

$$(Pt),H_2 \;\Big|\; \text{Solution} \;\Big|\; \text{Reference Electrode}$$

was followed on the recorder while a glass electrode was placed in the cell it could be seen that the hydrogen electrode was not disturbed by the transfer procedure. In between experimental runs the cells were cleaned by treatment with alcohol-nitric acid mixture after removal of most of the grease from the taps with cotton wool moistened with benzene. They were then thoroughly rinsed and soaked for a period in warm water and finally rinsed with distilled water and dried in an oven. All other glass-ware was periodically cleaned in the same way.

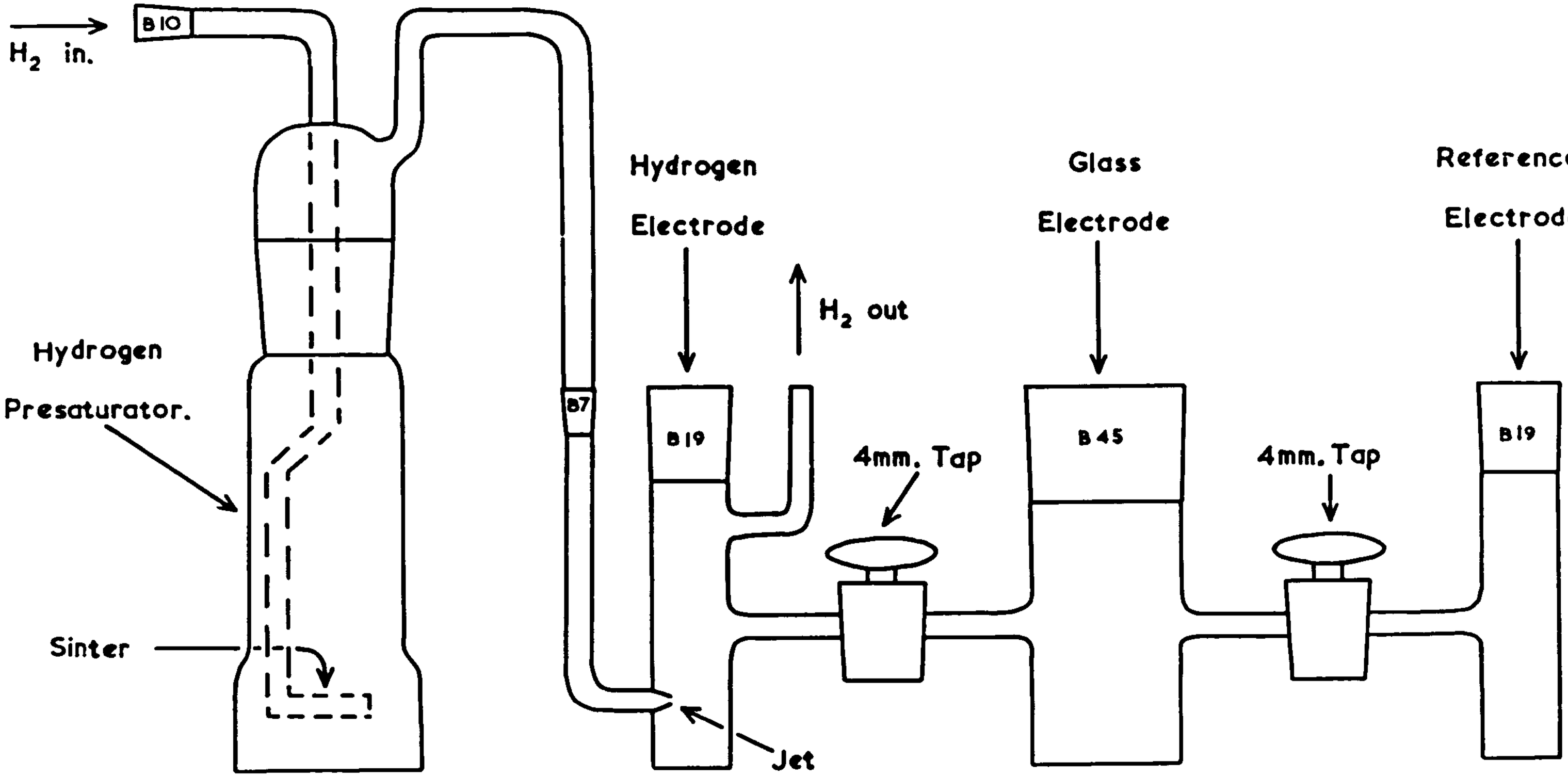


Fig. 1 Pyrex Cell used for Transfer Experiments.

4.2. Solutions.

Solutions were prepared using deionised water which was produced from distilled water by an ion exchange column of mixed resins (Permutit Zeo-Karb 225 and De-Acidite FF). The quality of the water was checked with a conductivity cell on the outlet of the column and the specific conductivity was not allowed to rise above 2×10^{-7} $ohm^{-1}cm^{-1}$. Whenever possible 'Analar' reagents were used without further purification. All solutions were prepared by weight and the appropriate buoyancy corrections were made. They were stored in 2-litre pyrex flasks fitted with ground glass stoppers, unless otherwise stated.

'Analar' hydrochloric acid was used to prepare constant boiling HCl by the method of Foulk and Hollingsworth.[58] Prior to distillation, the acid was saturated with chlorine to convert any HBr or HI to the free halogen. It was then boiled under reflux and tested for free chlorine with CdI_2 solution as described in the 'Analar' handbook. 'Analar' HBr was also distilled to obtain the constant boiling fraction;[59] however since in this case there is very little data for the variation of the composition of the distillate with pressure, the acid was also standardised by titration. The acid was supplied by the manufacturer in brown bottles and was found to be quite yellow in colour. The impurity was partly bromine, which was expelled in the early part of the distillation, and partly some involatile material, probably resulting from attack of the glass, the distillate being quite

colourless after the bromine had been removed. 'Analar' sulphuric acid was used to make stock solutions which were standardised against hydrochloric acid by weight titrations against sodium hydroxide solution, using methyl red and/or bromocresol purple. The hydrobromic acid was standardised in the same way.

Acetate buffers with added chloride were prepared from 'Analar' acetic acid and either, 'Analar' sodium acetate ($CH_3COONa,3H_2O$) and sodium chloride or, reagent grade potassium acetate and 'Analar' potassium chloride. The acetic acid was standardised in the manner described above for the standardisation of sulphuric acid. Acetate buffers with added sodium chloride and either sodium fluoride or magnesium sulphate were prepared using 'Analar' NaF or $MgSO_4,7H_2O$. The solutions with added sodium fluoride were stored in polythene containers.

Alkaline solutions (pH >7) containing inorganic cations were made up as follows. Solutions of pH less than 11 were prepared by the addition of salts to tris-(hydroxymethyl)-aminomethane ('Tris'), ethanolamine, and in one case borax, buffers and those of higher pH were mixtures of hydroxides and the corresponding chlorides. 'Analar' NaCl, KCl, KBr, Li_2SO_4,H_2O, $MgSO_4,7H_2O$ and $Na_2B_4O_7,10H_2O$ were used for this purpose. Reagent grade tris - a white crystalline solid - was recrystallised from alcohol-water mixtures by a method similar to that of Fossum, Markunas and Riddick,[60] and reagent grade ethanolamine - a colourless oily liquid B.P. 171°C. - was purified by distillation at atmospheric pressure and collection of the middle

fraction, as recommended by Bates and Pinching.[61] However since the method of testing the glass electrode was direct comparison with hydrogen electrodes in the same solutions, it was decided that the reagent grade materials could be used without further purification provided that the e.m.f's. of cells:

$$(Pt),H_2 \;\big|\; \text{Solution} \;\big|\; \text{Reference Electrode}$$

were stable and no anomalous results were obtained. For both bases, the reagent grade material was standardised by titration against hydrochloric acid using bromocresol purple (pH of colour change 3.8 - 5.4) as indicator and was found to be 100.0 ± 0.3% pure.

For sodium solutions of high pH, carbonate-free 1.00N sodium hydroxide supplied in polythene containers by B.D.H. was used as a stock solution. Deionised water was collected in a pyrex flask under CO_2-free conditions and the required solutions were made up from this water and the stock solution under nitrogen in the air thermostat. The required amounts of 'Analar' sodium chloride were then added also under nitrogen. The concentration of the commercial sodium hydroxide solution was checked by the preparation of a standard solution in the manner just described and weight titration of this solution with hydrochloric acid. Lithium solutions of high pH were prepared from lithium hydroxide and hydrochloric acid since lithium chloride is deliquescent. Reagent grade lithium hydroxide ($LiOH,H_2O$) was used without further purification. In this case the principal impurity is 1% of lithium carbonate and although it is possible to remove this it was felt that this was not necessary in view of the nature of the experimental method,

particularly as the lithium hydroxide was a crystalline non-deliquescent solid. Although the lithium hydroxide already contained some carbonate, the solutions were again prepared under nitrogen to prevent further introduction of carbon dioxide.

One solution of high pH was prepared from tetraethylammonium hydroxide and the corresponding bromide. A reagent grade solution of the hydroxide was used without any purification since purification of the tetra-alkylammonium hydroxides is known to be difficult. As will be explained in Section 6.1., when the results obtained with this solution are discussed, there was reason to believe that this reagent grade material contained some impurities. The tetraethylammonium bromide was purified by recrystallisation from alcohol-water mixture. The nitrogen used to exclude carbon dioxide from the solutions of high pH was obtained from cylinders and also by evaporation of liquid nitrogen prepared from air after removal of carbon dioxide.

4.3. Reference Electrodes.

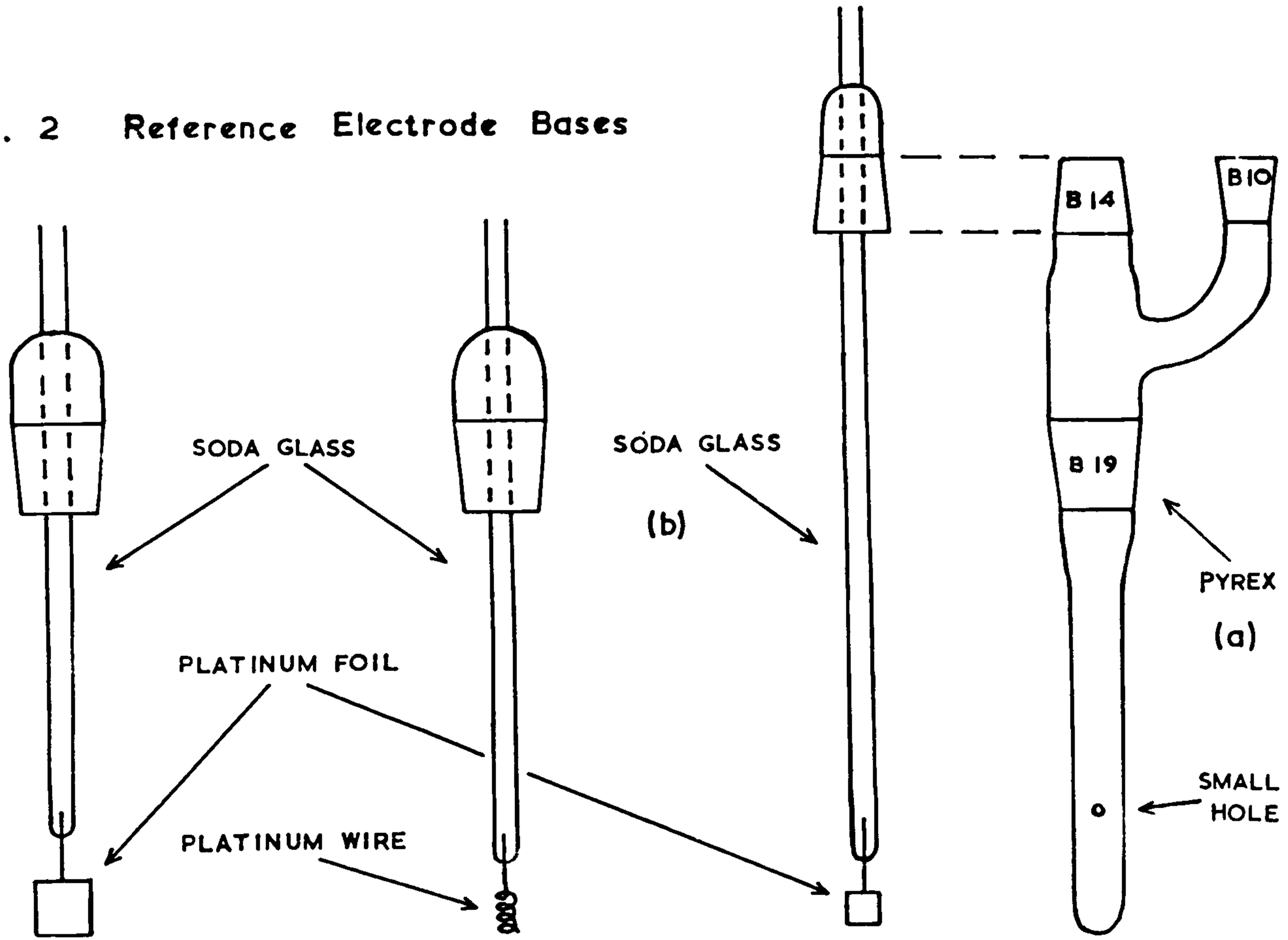
The Hydrogen Electrode: Hydrogen gas from a cylinder was passed over copper turnings contained in a silica tube and heated to about 500°C. in a furnace. It was then led through a column about 6" high packed with potassium hydroxide pellets and this was followed by a mercury safety blow-off. Before entering a cell, the gas was bubbled through a presaturator maintained at the same temperature in the air thermostat. This consisted of a gas wash-bottle fitted with a sintered disc on the inlet tube as shown in figure I and containing a portion of the cell solution. The hydrogen was supplied to the cells through a jet 1mm. in diameter at the rate of about two bubbles per second and was led from the cells outside the air thermostat by means of glass and PVC (Polyvinyl chloride) tubing 1-2 feet in length. Except for the presaturators which were fitted with ground glass joints, the components of the gas train were connected by lengths of glass tubing joined with tight-fitting PVC sleeves. These sleeves were renewed periodically in order to reduce the risk of contamination by oxygen and carbon dioxide from the atmosphere. The ground glass joints were greased and held together by rubber bands.

The electrode bases consisted of a piece of platinum foil 0.003" thick and 1cm. square spot welded close to the centre of one edge to about 2cm. of 0.021" diameter platinum wire. The wire was sealed into the end of a soda glass tube 0.2" in diameter which was attached to a B.19 ground glass

cone as shown in figure 2.1. Electrical contact was made with a small amount of mercury in the bottom of this tube. The platinum spades were cleaned by immersion in a warm mixture of 1 volume conc. HNO_3 1 volume conc. HCl and 4 volumes of distilled water either for a few minutes or until all the old platinium black had been removed (if the base had been used previously). After thoroughly rinsing them in distilled water they were platinised in a 2% solution of platinic chloride in 2m hydrochloric acid (without added lead acetate) with a current of 30mA for 15-20 minutes as recommended by Hills and Ives.[62] The completed electrodes were stored in deionised water when not in use. The bias potentials were usually not greater than 0.02mV and any electrode with a bias potential greater than 0.05mV was rejected. Readings of the barometric pressure were made during experimental runs to enable the e.m.f. values from cells involving the hydrogen electrode to be corrected to 1 atmosphere of hydrogen in the normal way, making allowance for the vapour pressure of the solution. No correction was made for the excess pressure in the hydrogen gas at the point of entry into the solution since this is negligible when e.m.f. measurements are not required with an accuracy greater than 0.1mV.[63]

Silver-Silver Halide Electrodes: Silver-silver chloride and silver-silver bromide electrodes of the thermal electrolytic type were prepared according to the method described by Bates.[64] The electrode bases consisted of a soda glass tube diameter 0.2" either sealed into a 8.19 ground glass stopper as

Fig. 2 Reference Electrode Bases



1. Hydrogen.

2. Silver-Silver Halide

3. Mercury-Mercurous Sulphate

shown in figure 2.2 or attached to a close-fitting B.19 polythene stopper. Into the lower end of the tube was sealed a 2" length of platinum wire 0.021" in diameter which was bent into a coil of about the same diameter as the glass stem. Electrical contact was made with a pool of mercury inside the stem. The platinum spirals were cleaned by immersion in 1 volume of conc. HCl, 1 volume of conc. HNO_3 and 1 volume of distilled water.

The silver oxide was prepared using solutions of 'Analar' sodium hydroxide and silver nitrate having "an exceptionally high degree of purity" supplied by Johnson Matthey Chemicals Limited. The oxide was washed about 30 times with deionised water and then applied as a paste to the platinum spirals. The bases were then placed in the entrance to a furnace which was allowed to heat up slowly to about 500°C. After the silver had been heated for about 15 minutes, the furnace was switched off and the bases were left in place while it cooled. This process was repeated until the spiral was covered with a ball of porous silver about 0.3" in diameter.

The halide was formed on the surface of the silver by anodic polarisation in a cell containing the appropriate acid using a platinum spade as cathode and a current of 10mA for 45 minutes. The electrodes were stored in approximately 0.1m acid. Their bias potentials were measured and any electrodes whose bias potentials differed from the average of the group by more than 0.1mV were discarded. When the silver-silver bromide electrodes were used in 5m and 11m HBr solutions they tended to turn white, apparently due to the dissolution of the silver bromide. However this was largely

prevented by the addition of a small amount of solid silver bromide to the silver-silver bromide electrode compartment of the cell.

When the hydrogen and silver-silver halide electrodes were used in alkaline solutions of high pH their stems were coated with Bedacryl 122X (a polymethacrylic ester) to prevent attack of the soda glass by the solution. This resin was supplied as a 40% solution in xylene by Imperial Chemical Industries Ltd. and the stems of the electrodes were painted with this solution and then left to dry. The hydroxide solutions did not attack the Bedacryl as was shown by the following experiment. Glass plates were coated with the resin and left for several days in contact with normal caustic soda solution. The Bedacryl surface was subsequently examined by electron microscopy and no signs of attack were detected.

Mercury-Mercurous Sulphate Electrodes: These were prepared, using the flowing anode method to obtain the mercurous sulphate, described by Beck, Dobson and Wynne-Jones.[65] Twice distilled mercury was allowed to pass from a separating funnel fitted with a capillary tube into molar sulphuric acid contained in a second funnel, the lower end of the capillary tube being below the surface of the acid. A platinum cathode was placed in the acid and a platinum wire sealed into the capillary tube was used to make contact with the mercury anode. The product was a mixture of mercury and mercurous sulphate, from which the excess mercury was removed, and was stored in a pyrex bottle out of direct sunlight. Samples for individual electrodes were

removed with a dropper and were placed in test tubes fitted with ground glass stoppers. They were then washed thoroughly by decantation with several portions of the appropriate solution.

The electrode base, similar to that used by Beck, Dobson and Wynne-Jones[65] is shown in figure 2.3. The mercury and mercurous sulphate were contained in the bottom of the electrode vessel (a) which was made from pyrex glass. This vessel had a hole 1mm. in diameter just above the level of the electrode material, to provide contact between the electrode and the cell solution. Electrical contact with the mercury was made with a platinum spade about 5mm. square sealed into the end of a soda glass tube 0.2" in diameter (b). This tube was inserted at the top of the electrode vessel (a) and was held firmly in position by the B14 ground glass joint shown in the diagram. The platinum was connected to the electrical measuring equipment in the same way as for the other reference electrodes.

Before use, both parts of the electrode base were cleaned in alcohol-nitric acid mixture and the platinum contact was cleaned in a mixture of nitric and hydrochloric acids as described for the other reference electrodes. To prepare an electrode, the platinum contact was placed in the electrode vessel and completely covered by twice distilled mercury. Then, using a dropper, the mercury-mercurous sulphate mixture was added down the side arm as a slurry in sulphuric acid until the mercury was covered by a layer about 0.2" thick. Finally the side arm was closed with a B10 stopper and the electrode was stored in sulphuric acid solution of the same molality. Any electrodes whose bias potentials were greater than 0.1mV were discarded.

4.4. Glass Electrodes.

All experiments were carried out with new commercial glass electrodes. Details of the pH responsive electrodes are given in table 4-1 and details of the cation responsive electrodes were given earlier in section 3.1. Most manufacturers refuse to disclose the exact composition of their electrode glasses. However glass membranes from some of the types of pH responsive electrode tested in this work had previously been analysed in the department by flame photometry and the following data were obtained.

Type	Mole %				
	Na_2O	Li_2O	Cs_2O	CaO	SiO_2 (by difference)
Jena H	21.3	-	-	7.3	71.4
Jena HA	-	20.8	1.5	1.3	76.4
E.I.L. GHS33	-	20.3	0.2	2.6	76.9

(The figures for CaO may be unreliable)

The Beckman E2 electrode is stated[66] to have a membrane composed of a Li_2O, BaO, SiO_2 glass and that of the E.I.L. GG33 electrode is stated by the manufacturer to be MacInnes-Dole glass. There appears to be no information available for the composition of the other glass electrodes tested. However the remaining pH responsive electrodes (Radiometer, Pye Ingold and Corning) are thought to have lithia glasses.

Hence on the basis of glass composition it was not possible to do more

TABLE 4.1.

Details of pH Responsive Glass Electrodes Used.

Manufacturer	Type No.	Manufacturer's Description			Electrode Numbers.
		pH Range	Temperature Range	Comments	
Electronic Instruments Limited (E.I.L.) Richmond, England	GG 33	0 - 10	10^{o} - 45^{o} C	Standard	1,5,6,8, 12,14.
	GHS 33	0 - 14	0^{o} - 70^{o}C	All purpose	11, 18
Beckman, Fullerton, California	41260	0 - 14	15^{o} - 80^{o} C	Glass Type E2 (Blue)	3, 19
Corning Instruments, Medfield, Massachusetts	476022	0 - 14	-5^{o} - 100^{o} C	Triple Purpose	27, 30
Jena Glaswerk, Mainz, Germany	HA 9401	1 - 14	0^{o} - 70^{o} C	High Alkaline	22, 29
	H 9214	0 - 11	-10^{o} - 50^{o} C	Highly Resistant	9, 21
Pye Ingold, Cambridge	201	0 - 13	0^{o} - 70^{o} C	Standard	10, 15
Radiometer, Denmark	G 202 B	0 - 14	20^{o} - 60^{o} C	General Purpose	4, 17
	G 202 C	0 - 12	0^{o} - 60^{o} C	General Purpose	7, 16

than divide the electrodes broadly into two groups, a) those with soda glass membranes and b) those with membranes made from lithia glasses. Nevertheless it was clear that the behaviour of glass electrodes depends not only on the nature of the major components of the glass but also to a large extent upon the relative amounts of these components. The response characteristics are also dependent upon the nature and amounts of other components present perhaps as only a few mole %. For example, the three types of Beckman electrode, General Purpose, Type E2 and Amber are all stated to have Li_2O, BaO, SiO_2 glass membranes[66] but they vary considerably in their properties.

All the glass electrodes tested except those of type Jena H already contained an inner reference electrode and solution when they were received from the manufacturers. However for some types the composition of the inner solution and reference electrode were not known, although in these cases it was usually possible to suggest the composition from the observed potentials of the electrodes relative to the hydrogen electrode in solutions where the glass electrodes showed no errors. The available information for the pH responsive electrodes is summarised in Table 4-2. All the glass electrodes which were supplied complete with inner reference electrode had screened leads and were fitted with coaxial plugs before use.

The two Jena H electrodes were received simply in the form of an empty glass stem with the pH sensitive membrane blown as a bulb on the end and they were therefore fitted with internal reference electrodes before use.

TABLE 4.2. Inner Reference Systems of Glass Electrodes

Type of Electrode	Potential (Volts)	Inner Reference System a) Electrode	b) Solution	Reference
Corning	0.68	Ag - AgCl	Phosphate Buffer + Chloride	68
Jena HA	0.48	Ag - AgCl	Acetate Buffer + Chloride	
E.I.L. GG 33	0.38 - 0.42	Ag - AgCl	0.1m HCl	69
E.I.L. GHS 33	0.36	Probably the same as GG 33		
Beckman E2	0.66	Probably:- Ag - AgCl	Phosphate Buffer	67
Pye Ingold	0.35	In view of the observed potential probably:- Ag - AgCl	0.1m HCl	
Radiometer Types 8 and C	0.61 - 0.63	Ag - AgCl	Sodium Citrate + HCl pH 4.7	70
Jena H	0.36 - 0.40	Ag - AgCl	0.1m HCl	

Approximately 0.1m HCl and silver-silver chloride electrodes of the thermal-electrolytic type were used for this purpose. Electrical connection was made with Transradio coaxial cable NO3/50 having an outer diameter of 2mm. and fitted with a coaxial plug. The screen of the coaxial cable was removed for a distance of about $1\frac{1}{2}$" from the end, and the central copper lead was attached to the platinum wire for the silver-silver chloride electrode using high melting solder. The platinum wire was then sealed into the glass supporting tube and the silver-silver electrode was then prepared in the manner already described. One of these soldered joints subsequently became disconnected after the platinum had been sealed into the glass tube and for this electrode a mercury contact had to be used. However both arrangements gave satisfactory results. As received from the manufacturer these electrodes had the outer surfaces of their pH sensitive membranes coated with paraffin wax. In order to dissolve this away, the completed electrodes were left for a period with their bulbs immersed in either carbon tetrachloride or benzene.

Each electrode was mounted in a B45 polythene stopper with a circular hole, $\frac{3}{4}$" in diameter, drilled down the centre to receive it, similar to those used by Caudle.[1] The space between the electrode stem and the polythene bung was packed with polythene turnings and finally filled with paraffin wax to hold the electrode firmly in position. In some experiments the electrode stems were freshly coated with a thin layer of wax as recommended by Caudle. The wax used both for this purpose and for mounting the electrodes was Shell "Stanlow fully refined grade" (125-130^{o}F. E.M.P.).

Before use, the membranes of the pH responsive electrodes were conditioned for at least 24 hours in deionised water and the electrodes were also stored with their membranes in water in between experimental measurements. The cation responsive electrodes were normally conditioned and stored in tris buffers containing 1 molal sodium or potassium chloride. However the pH response of some of these electrodes was also examined before they were tested in solutions of the alkali metal ions. The electrodes were therefore initially conditioned and stored in deionised water. It is recommended that cation responsive electrodes like pH responsive electrodes should be kept moist and Mattock[40] observed that if BH68 (GNA 33) electrodes were allowed to dry out their response to sodium suffered markedly.

At the end of the work, the d.c. resistances of all but two of the electrodes (two electrodes were no longer in existence) were measured using a circuit similar to that of Eckfeldt and Perley,[71] and Simon and Wegmann,[72] which is also described by Bates.[74] The necessary standard resistances were contained in the sealed metal switch-box described in section 4.1. and the values obtained for the resistances of the glass electrodes are given in the appendix.

CHAPTER 5

Experimental Techniques and Procedures

This chapter is mainly concerned with the procedures used in the present work for testing glass electrodes and analysing the data obtained. However, in order to explain the choice of cells and experimental procedure, the basic methods available will first of all be discussed in sections 5.1 and 5.2, since certain significant factors have sometimes been overlooked in the past. In section 5.3 the actual procedures and experimental techniques used in previous investigations will be reviewed in the light of this discussion and it will be observed that in some cases the experimental techniques also left something to be desired. Finally in section 5.4, the experimental procedure used in the present work will be described in detail and the methods which have been used for analysing and presenting the e.m.f. data will be explained.

5.1. Cells for Testing Glass Electrodes

The first stage in the development of a glass electrode is the determination of the composition of the membrane glass which has the most favourable response for the ion in question. The selection of a suitable glass usually requires an extensive investigation involving a large number of electrodes of different glass composition, and it is therefore important to have a fast and convenient method of examining the main features of the

response. A saturated calomel reference electrode is usually used for this purpose but the resultant cell is not suitable for precise measurements since it contains a liquid junction.

Once glasses, which are likely to be suitable for the fabrication of electrodes responsive to the ion in question, have been selected by this method, further electrodes may be prepared for more rigorous testing. This is best carried out by comparison of the glass electrodes with other electrodes responsive to the same ion. For example, pH responsive glass electrodes are tested against hydrogen electrodes and electrodes responsive to the alkali metal ions might be tested against amalgam electrodes, although in the latter case the method has not yet been applied. Both the hydrogen electrode and amalgam electrodes require much more elaborate experimental technique than the calomel electrode and are therefore more suitable for testing a relatively small number of electrodes but with greater accuracy. Alternatively glass electrodes may be tested using cells without liquid junction containing reference electrodes reversible to anions. This procedure has been used for both pH responsive and cation responsive electrodes. These more rigorous methods of testing will now be discussed.

It has been a common practise when comparing pH responsive glass electrodes with hydrogen electrodes to introduce a third electrode into the cell in order to provide a check upon the stability and reproducibility of the potential of the hydrogen electrode. A saturated calomel electrode has often been used for this purpose but this is not entirely satisfactory since

the cell:

$$\text{(Pt)}\ \ H_2\ (p)\ \Big|\ \text{Test Solution}\ \Big|\ \text{Sat. KCl}\ \Big|\ Hg_2Cl_2 - Hg \qquad (1)$$

where p is the partial pressure of hydrogen, then involves a liquid junction at which the potential may vary. Furthermore, unless precautions are taken to prevent it, potassium ions may diffuse from the saturated potassium chloride into the test solution and these will influence the magnitude of the errors shown by the glass electrodes in alkaline solutions. It is much preferable to use a reference electrode reversible to an ion, other than the hydrogen ion, in the test solution and thus avoid a liquid junction. Some investigators using the three electrode system (see, for example, references 11, 12 and 19) have in fact measured the e.m.f's. of cells 1 and 2:

$$\text{glass electrode}\ \Big|\ \text{Test Solution}\ \Big|\ \text{Sat. KCl}\ \Big|\ Hg_2Cl_2 - Hg \qquad (2)$$

and then obtained the e.m.f. (E_3) of cell 3:

$$\text{(Pt)}\ \ H_2\ (p)\ \Big|\ \text{Test Solution}\ \Big|\ \text{glass electrode}$$

from the difference. However this procedure is only satisfactory for precise work if the e.m.f's. of cells 1 and 2 are measured simultaneously, since otherwise an uncertainty is introduced due to possible fluctuation of the liquid junction potential. It is desirable therefore to measure E_3 directly.

Once E_3 has been measured either directly or indirectly it is necessary to have some means of determining the response of the glass electrode in the solution in question. Testing the response of any electrode, not necessarily a glass electrode, always involves the measurement of the e.m.f's. of at

least two cells. Two different procedures have been employed in the past when testing a pH responsive glass electrode using cell 3, and these will now be considered. It follows from the above that both these procedures involve, in addition to the measurement of E_3, the measurement of the e.m.f. of at least one other cell containing the glass electrode.

Some previous workers when testing pH responsive glass electrodes have regarded the e.m.f. (E_4) of the cell:

$$(Pt)\ H_2\ (1atm.) \mid \text{Test Solution} \mid \text{glass electrode} \qquad (4)$$

as having three parts: a) the theoretical e.m.f., b) the asymmetry potential of the glass electrode and c) the error in the hydrogen ion response of the glass electrode. The value of the theoretical e.m.f. (E_5) is dependent only upon the inner reference system of the glass electrode and is the e.m.f. which would be observed if the two sides of the glass membrane behaved as two identical hydrogen electrodes with the same partial pressure of hydrogen gas. For example, if the glass bulb contains 0.1m HCl and a silver-silver chloride electrode then the theoretical e.m.f. would be the e.m.f. of the cell:

$$(Pt)\ H_2\ (1atm.) \mid \text{Test Solution} \mid H_2\ (p)\ Pt - Pt\ (p)\ H_2 \mid 0.1m\ HCl \mid Ag\text{-}AgCl$$

which would be equal to the e.m.f. of the cell:

$$(Pt)\ H_2\ (1atm.) \mid 0.1m\ HCl \mid AgCl\text{-}Ag \qquad (5)$$

i.e. 0.3524 volts at 25°C. The asymmetry potential (E_6) of a glass electrode is defined as the e.m.f. which would be observed between two identical reference electrodes placed in the same solution on either side of the glass

membrane. It might, for example, be determined using the cell:

$$\text{Ag-AgCl} \;\big|\; \text{0.1m HCl} \;\big|\; \text{glass} \;\big|\; \text{0.1m HCl} \;\big|\; \text{AgCl-Ag} \qquad (6)$$

In many previous investigations, the asymmetry potential has been considered to be constant for the period of an experimental run. Whether this assumption is justified will be considered later but it will be accepted for the present in order to simplify the discussion. The glass electrode error (ΔE) in the test solution of cell 4 is given by:

$$\Delta E = E_4 - E_5 - E_6$$

This type of approach may be illustrated by the work of MacInnes and Belcher.[13] These investigators corrected the e.m.f's. of cells of type 3 for the deviation of the partial pressure of hydrogen (p) from one atmosphere to give the e.m.f's. (E_4) of the corresponding cells of type 4. they then corrected these values for the asymmetry potentials of their glass electrodes which had previously been measured. Provided the glass electrode showed the true hydrogen ion response (i.e. $\Delta E = 0$), the corrected e.m.f's. were equal to the theoretical e.m.f., E_5, which had also been determined. Any deviation from this value was therefore the error of the glass electrode.

$$\text{i.e.} \quad E_4 = E_5 + E_6 + \Delta E$$

$$\Delta E = (E_4 - E_6) - E_5 \qquad \text{or if } \Delta E = 0 :- \; E_4 - E_6 = E_5$$

Hence this method of determining the error of a glass electrode requires a measurement of the asymmetry potential in addition to E_3. The theoretical e.m.f. is usually already known.

As will now be seen, it is possible to determine the error of a glass electrode by a much simpler procedure than the one just described. This second procedure makes use of solutions in which the glass electrode shows the correct pH response. These will be termed standard solutions. However before the procedure is explained it is necessary to consider carefully what is meant when it is stated that a glass electrode shows the 'correct pH response' since this has not been fully considered in the past.

If a glass electrode responds in the same manner as the hydrogen electrode then all cells:

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Solution} \ \Big|\ \text{glass electrode}$$

should have the same e.m.f. irrespective of the nature of the solution. In fact it has been shown[1,2,30,31] that glass electrodes may agree with the hydrogen electrode to 0.1mV or better provided that the solutions and experimental technique are correctly chosen. However it is found that some electrodes show small errors even in the intermediate pH range. These errors are random and independent of the nature of the solution provided it is well buffered,[75] and hence the pH apparently is the only feature of the solution which influences the electrode potential. Such a glass electrode shows a pH response in this range but the precision is limited to $\pm x$, where x is characteristic of the electrode (x is usually less than 1mV). In acid and alkaline solutions, errors are observed which are outside the limits of error, $\pm x$, of the pH response of the electrode and are dependent upon factors such as the nature and concentration of the other ions in the solution.

These will be regarded as deviations from the pH response of the electrode and a standard solution will be defined as one in which the glass electrode in question shows the correct pH response within the limits of its inherent reproducibility, $\pm x$, that is to say, the pH is the only feature of the solution that influences the electrode potential.

It follows from the above paragraph that the precision with which a glass electrode may be said to agree with the hydrogen electrode in the intermediate pH range is determined either by the precision of the experimental method or by the glass electrode itself. This may be illustrated by considering the results which might be obtained when testing two different electrodes in this pH range using an experimental method accurate to 0.1mV.

Electrode A. Erratic and agrees with the hydrogen electrode only to ±0.5mV when tested in a number of different solutions.

Electrode B. Agrees with the hydrogen electrode to 0.1mV.

A standard solution for electrode A is therefore one in which it agrees with the hydrogen electrode to ±0.5mV and hence is defined in terms of the performance precision of the glass electrode itself. On the other hand a standard solution for electrode B is one in which it agrees with the hydrogen electrode within the accuracy of the experimental method. It is possible that if electrode B were tested with greater precision it would be found to show even closer agreement with the hydrogen electrode.

From the above definition of a standard solution, the e.m.f. (E_7) of the cell:

(Pt) H_2 (p) | Standard Solution | glass electrode (7)

is independent of the chemical composition of the solution. It is constant, either within the limitation of the glass electrode or within the experimental error, provided the partial pressure of the hydrogen (p), and the asymmetry potential of the glass electrode are constant. If p is one atmosphere then:

$$E_7 = E_5 + E_6$$

If E_3 is also measured, then provided the partial pressure of hydrogen and the asymmetry potential of the glass electrode are the same in both cells, the error of the glass electrode in the test solution is given by:

$$\Delta E = E_3 - E_7$$

Hence, in order to determine the error of a glass electrode by this method it is not necessary to correct the observed e.m.f's. to the values corresponding to one atmosphere of hydrogen; in fact the partial pressure of hydrogen need not be known. However, if this partial pressure differs between the two cells, perhaps because the two solutions have different vapour pressures, then it is necessary to know this difference.

It might appear at first sight that this procedure is more complex than the one involving measurement of the asymmetry potential, since it is necessary first of all to identify some standard solutions for the glass electrode in question, and this requires e.m.f. measurements on at least two different cells of type 7. However, it should be noted that if the asymmetry potential is measured, it is essential that the solution employed should be a standard solution. Hence this method also requires that some

standard solutions should previously have been established. It is, in fact, entirely unnecessary to obtain separate values of the asymmetry potential, E_6, and the theoretical e.m.f., E_5, but clearly if the theoretical e.m.f. is known the asymmetry potential can be calculated from E_7 if the partial pressure of hydrogen is measured. By measuring the e.m.f. E_7, one is of course calibrating the glass electrode directly against the hydrogen electrode and this e.m.f. will therefore be called the calibration e.m.f.

This method of calibrating a glass electrode was used by Dole[11,12], although it should be noted that in these publications the term 'theoretical e.m.f.' was applied to cells of type 7 and not as defined here. The e.m.f. of cell 7 was determined for each glass electrode using buffer solutions in the intermediate pH range and checking that the value was independent of the solution. However, Dole later suggested that this procedure for obtaining E_7 was dangerous since there may be a constant error in the value which would not be detected. He presumably had in mind errors such as would be caused by electrical leakage at the glass electrode. However, experience in the present work has suggested that if there is some electrical fault at the glass electrode it will be revealed using this method. This is to be expected, since although E_7 is independent of the nature of the standard solution, the potentials at the hydrogen and glass electrodes will of course depend upon the pH, and hence any error due to electrical leakage at the glass electrode will vary when the solution is changed.

Some previous workers have tested the response of glass electrodes using

silver-silver chloride reference electrodes placed directly in the same solutions. When this procedure is applied, the e.m.f. differences for pairs of cells:

$$\text{glass electrode} \;\Big|\; \text{Solution } (Cl^-) \;\Big|\; \text{AgCl-Ag} \qquad (8)$$

are compared, either with values calculated using activity coefficient data, or with known values for the corresponding cells in which the glass electrode is replaced by another electrode responsive to the same ion. This method is therefore perfectly satisfactory for precise work since the cell does not contain any liquid junction. Covington and Prue[30] used this procedure for testing pH responsive glass electrodes and other workers[39,50-52] have used it to test cation responsive electrodes.

In this section the cells suitable for investigating the response of glass electrodes have been discussed and it has been pointed out that for precise work the cell chosen should not contain a liquid junction. The most satisfactory cell, which is appropriate for precise work, is that in which the glass electrode is compared directly with another electrode reversible to the same cation, and it is desirable to check the correct functioning of this electrode with a third electrode reversible to another ion in the test solution. This arrangement has been used in the present work for testing pH responsive electrodes. It is not necessary to measure the asymmetry potential of a glass electrode in order to test its response by this method, but preferable simply to calibrate the electrode directly against a hydrogen electrode using a standard solution. It is sometimes desired to avoid the

use of a reference electrode reversible to the same ion as the glass electrode under test on account of the elaborate experimental technique involved. In this case the glass electrode may be tested using an electrode reversible to an anion in the test solution, provided that the necessary e.m.f. or activity coefficient data are available. This arrangement has been used in the present work for testing cation responsive electrodes.

5.2. Time Dependence of Glass Electrode Potentials.

In the early days of the development of glass electrodes it was probably hoped that it would be possible to prepare electrodes whose asymmetry potentials would become completely constant after the initial conditioning period. For example, one of the requirements of a good glass electrode listed by Hughes[3] was that it "should rapidly reach a constant asymmetry e.m.f." and MacInnes and Dole[4] measured the asymmetry potentials of their electrodes, because they had found that when the asymmetry potential was large, it was also likely to be varying and require frequent redetermination. However it has been found that Hughes' requirement cannot be met in practice. Even under favourable conditions the asymmetry potentials of the best electrodes vary slowly with time and may change significantly from one day to the next. This was apparently realised as early as 1931 since MacInnes and Belcher[13] report a number of results for the same electrode, presumably obtained on different days, with different values for its asymmetry potential. Nevertheless, in several subsequent investigations, both with pH responsive glass electrodes and those which respond to other cations, the asymmetry potentials were regarded as constant for the period of an experimental run.

In recent years, however, it has been realised[1,31] that when the e.m.f. of a cell of type 7 is measured with a precision of better than about ± 0.01 of a pH unit, it is often impossible to record a unique value since the e.m.f.

is changing slowly with time. If the partial pressure of hydrogen is constant, this e.m.f. variation is due to a slow change of the asymmetry potential of the glass electrode and it may be allowed for by the transfer and extrapolation procedure introduced by Covington and Prue.[30] Using this procedure, a glass electrode in a cell of type 7, is transferred with washing to a similar cell, containing a second standard solution and a hydrogen electrode which has already come to equilibrium. If the glass electrode agrees with the hydrogen electrode within the precision of the experimental method, the e.m.f. variations observed for the two cells extrapolate to the same value at the instant of transfer of the glass electrode, and the asymmetry potential has the same value for both cells at this point. The foregoing remarks are applicable in principle to any cell involving a glass electrode and a standard solution, provided it does not contain a liquid junction (e.g. cell 8). In fact the transfer and extrapolation procedure was first applied by Covington and Prue to cells having silver-silver chloride reference electrodes. Also although these principles have been introduced by considering a pH responsive electrode it should be noted that they are equally relevant to glass electrodes which are primarily responsive to other cations.

It has been found however, both in the present investigation and by Caudle, that when a glass electrode is transferred with washing between a pair of cells:

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Solution} \ \Big|\ \text{glass electrode}$$

containing pre-equilibrated hydrogen electrodes, the observed variations of

e.m.f. do not always extrapolate to the same value at the instant of transfer. The difference between the extrapolated values is referred to as the instantaneous error. When a glass electrode gives the same e.m.f. in two cells at the instant of transfer between them, the instantaneous error is said to be zero and any subsequent change of e.m.f. for the second cell is regarded as a change of asymmetry potential. If the instantaneous error is not zero and the e.m.f. for the second cell changes with time, then the electrode is regarded as showing a time dependent error, which is defined as the difference between the e.m.f. at a certain time for the second cell and the final e.m.f. for the first solution. The error corresponding to the first e.m.f. measurement in the test solution will be called the initial error and that corresponding to the last observed e.m.f. in the second solution will be called the final error. This method of describing the errors shown by glass electrodes is illustrated in figure 3. As will be seen in Section 5.4, a rapid change of e.m.f. is often observed immediately after an electrode is transferred to a new solution. It is then impossible to carry out the extrapolation to obtain the instantaneous error and only the initial error can be recorded.

Since the asymmetry potential of a glass electrode is no longer to be regarded as constant, it is necessary to reconsider how standard solutions for an electrode are identified in practice. A standard solution was defined as one in which a glass electrode shows pH response only, but it was pointed out that the precision of this pH response might be limited by the glass

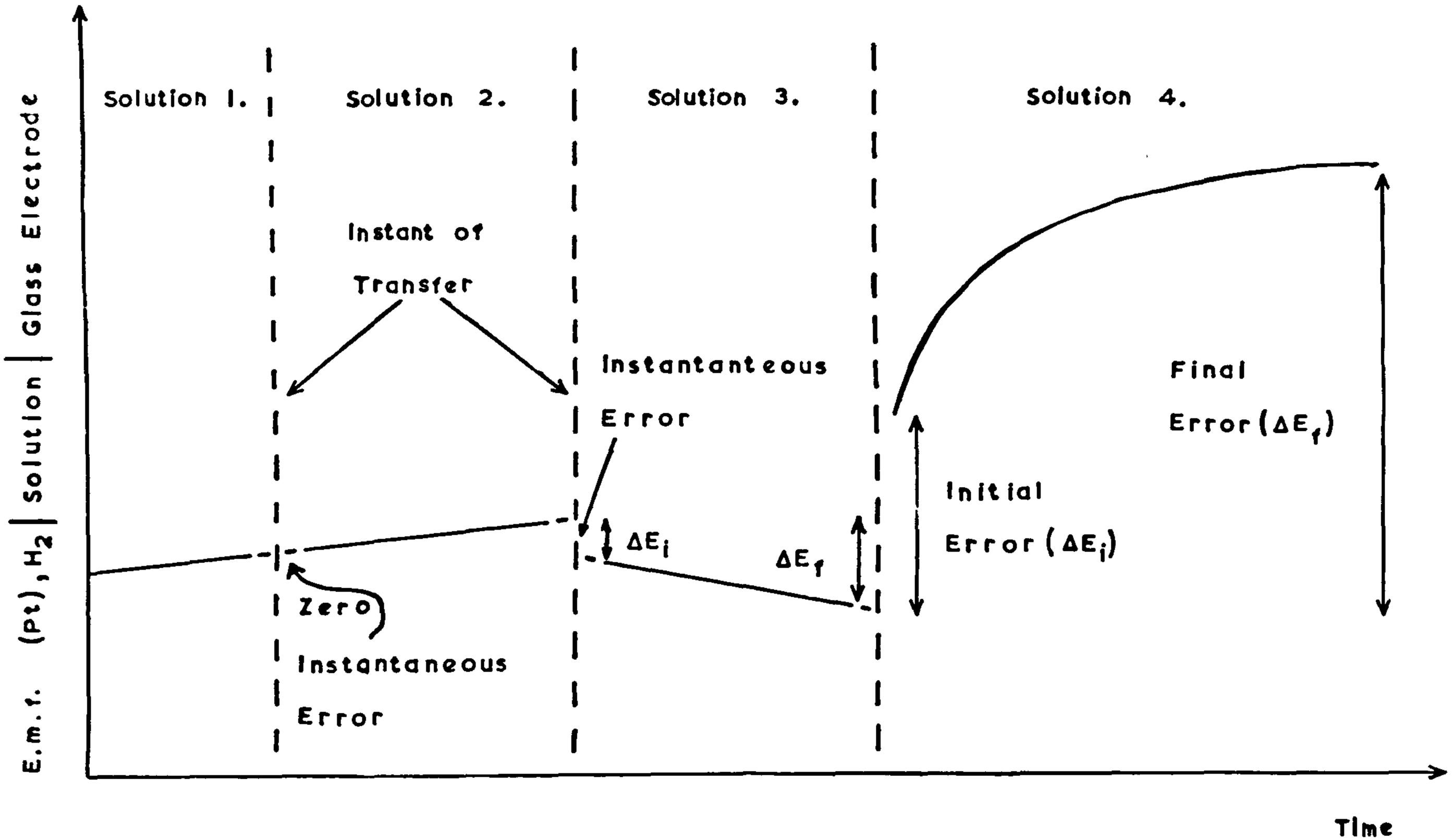


Fig. 3 DESCRIPTION OF GLASS ELECTRODE ERRORS

electrode itself. Hence although some electrodes may show no error, within the precision of the experimental method, at the instant of transfer between two solutions of intermediate pH, others show small instantaneous errors which are random and independent of the nature of the solution. Therefore if the glass electrode in the cell:

$$(Pt)\ H_2\ (p) \quad \Big| \quad \text{solution} \quad \Big| \quad \text{glass electrode}$$

is transferred with washing to similar cells containing pre-equilibrated hydrogen electrodes, and the instantaneous errors fall within the performance precision ($\pm x$) of the glass electrode in question, then the solutions may be regarded as standard solutions. With the best electrodes which agree with the hydrogen electrode within the precision of the experimental method, it can be observed that there is no discontinuity in the drift of e.m.f. on replacing one standard solution in cell 7 by another; i.e. by transferring the glass electrode between two such cells containing pre-equilibrated hydrogen electrodes.

In the present investigation, as in the work of Caudle, the e.m.f's. of glass electrode cells have been measured to 0.1mV. Hence, even when testing a glass electrode in standard solutions, it has been necessary to use the transfer technique of Covington and Prue, and take into account the time dependence of the e.m.f. Previous testing of glass electrodes at this level of accuracy has been limited to acid solutions, and one of the objects of the present work has been to test the performance precision of

the various electrodes in standard solutions covering a fairly wide pH range. Also these previous investigations involved only a relatively small number of different types of glass electrode, and several types not included in the earlier investigations have been tested here. The present work was also concerned with examination of the response of glass electrodes in solutions in which they show errors, particularly in the alkaline pH range. These errors are often time dependent and application of the transfer procedure enables the variation of the glass electrode potential to be observed immediately after placing the electrode in a test solution.

5.3. Experimental Techniques used in Previous Investigations.

As was noted earlier many previous investigators have regarded the asymmetry potentials of their glass electrodes as being constant for the period of an experimental run. Whether or not this assumption is reasonable depends upon the precision required, the length of time over which the asymmetry potentials were regarded as constant and the actual rate of change. The extent to which the asymmetry potential of an electrode changes with time largely depends upon the treatment which the electrode receives. If the electrode is allowed to become dry even for a short period, is disturbed mechanically, is polarised (perhaps to measure its resistance) or is placed in a solution where it shows a large error or one which involves a change of solvent, the asymmetry potential may change by several millivolts in a relatively short time. If on the other hand, the electrode is kept in contact with solutions having the same solvent which have only a mild effect upon it, such as standard solutions or solutions where only small errors are observed, the asymmetry potential often varies only slowly with time. For example, under these conditions, the asymmetry potential of an electrode will usually remain constant to within a few tenths of a millivolt over a period quite long enough to make e.m.f. measurements in several different solutions. Hence in favourable circumstances, the assumption that the asymmetry potential of an electrode is constant for the period of an experimental run will probably be justified if an accuracy of no better than about ±0.01 of a pH

unit is required. However if the electrode is used in acid or alkaline solutions where errors are observed then it is advisable to check the calibration in a standard solution in between measurements.

When glass electrodes are tested against calomel electrodes, it is reasonable to regard their asymmetry potentials as constant over short periods, since the precision of the experimental method is not high. For example, the method has been used in recent years by Eisenman et al.,[36] and by the Russians Nikolsky, Shultz and their collaborators,[38] for testing cation responsive glass electrodes, and the reproducibility of the e.m.f. measurements, which were made at room temperature, was ±5-10mV. This method of testing has also been used by MacInnes and Dole,[4] Ssokolov and Passinski[5] and Perley[7] for pH responsive glass electrodes. However, although much useful data has been obtained by this method, the precision is not comparable with that of the present work.

When measurements are made with a precision of better than about ±0.01 of a pH unit, the asymmetry potential of a glass electrode cannot be regarded as constant and the transfer and extrapolation procedure, described in the last section, should be applied. In the present work, it has sometimes been found that the calibration e.m.f. (E_7) and hence the asymmetry potential of a glass electrode is constant to 0.1mV for some time perhaps even as long as 2-3 hours. In this case the extrapolated e.m.f. at the instant of transfer is the same as the e.m.f. 5-10 minutes later and the extrapolation is in fact hardly necessary. However although the asymmetry potential may remain constant

to 0.1mV for some time it cannot be relied upon to do so.

Dole[11,12] was among the many previous workers who assumed the asymmetry potential of a glass electrode to be constant for the period of an experimental run. This was hardly justified since his measurements were made with a precision of ±0.1mV, however as a check he measured the e.m.f. (E_7) for his electrodes both at the beginning and at the end of a run. In the case of those electrodes for which he gives the experimental data in detail, the overall change was small, only 0.3mV. However, Dole states that this set of results were "particularly concordant and were perhaps the best that were obtained."

Sinclair and Martell[19] who tested glass electrodes in acid solutions also assumed that the asymmetry potentials of their electrodes were constant for the period of an experimental run. They stated that in dilute acid solutions the glass electrodes agreed with the hydrogen electrode to within ±0.2mV. However examination of their data suggests that larger differences were in fact obtained and these were probably due to variations of the glass electrode asymmetry potentials.

Simon and Wegmann[72,73] apparently also regarded the asymmetry potentials of their glass electrodes to be constant. These workers compared their glass electrodes with hydrogen electrodes placed in the same solutions but they used the indirect method with saturated calomel electrodes, since this enabled them to follow the variation of glass electrode potential before their hydrogen electrodes had come to equilibrium. As was pointed out in

section 5.1., this procedure involves an uncertainty due to possible fluctuation of the liquid junction potential. Their technique was to place the glass and other electrodes in the cell vessel and then to add the solution. Measurements were made in the order; phosphate buffer pH 6.86, borax buffer pH 9.18, tartrate buffer pH 3.56, phosphate buffer pH 6.86, 0.1M NaOH and 1.0M NaOH. Hence before the electrodes were tested in alkaline solutions they were, in effect, calibrated in the buffers. The measurements in the phosphate buffer were repeated in order to check the stability of the electrode potentials and this would provide some check upon the asymmetry potentials.

When one of the buffers was used there was a delay of 15 minutes between placing the solution in the cell and making the first e.m.f. measurement. This delay was apparently due to the need to allow the solution to reach the thermostat temperature. The sodium hydroxide solutions on the other hand had been previously placed in the thermostat to attain thermal equilibrium, but even when the cell contained one of these solutions, the first e.m.f. measurement was not made until 3-10 minutes after the glass electrode first came into contact with the solution. Hence, when investigating the time dependence of the alkaline errors, they were unable to follow the e.m.f. variation immediately after placing the electrode in the solution as was done in the present work.

Although they quoted the alkaline errors to 0.01 of a pH unit, there are two reasons why the data are not as accurate as this. Firstly, since

saturated calomel electrodes were in effect used, the observed variations of e.m.f. may have been due in part to changes in the liquid junction potential. From measurements of the hydrogen-calomel electrode e.m.f's. Simon and Wegmann estimated that variations of liquid junction potential were not greater than ±0.5mV. Secondly the experimental technique involved a delay between calibrating the electrodes in the phosphate buffer and first contact with the alkaline solution and during this time the asymmetry potentials of the electrodes might have changed. In the intermediate pH range a response of between 58.6 and 59.4mV per pH unit was regarded as being in agreement with the theoretical value of 59.16mV per pH unit, within the experimental error.

Schwabe and Glockner[20,21] measured the potentials of their glass electrodes directly against hydrogen electrodes placed in the same solutions. However, the only check on the stability and reproducibility of the potential of one of their hydrogen electrodes, was provided by a second hydrogen electrode. If a change in the composition of the solution took place during an experimental run, it is possible that the potential difference between the two hydrogen electrodes would not reflect it, if the solution in the region of each electrode changed to the same extent. The hydrogen gas was in fact dried by passing it through concentrated sulphuric acid and then it was apparently lead straight to the presaturator. If small droplets of sulphuric acid were carried over by the gas they could have caused solution composition changes, first in the presaturator and then in the cell itself.

Schwabe and Glockner used a standard acetate buffer and a mercury-mercurous acetate electrode as the internal reference system for their glass electrodes, and state[21] that the e.m.f's. of the cells:

$$\text{(Pt) } H_2 \;\Big|\; \text{Acid X} \;\Big|\; \text{glass} \;\Big|\; \begin{matrix}\text{0.1M HAc}\\ \text{0.1M NaAc}\end{matrix} \;\Big|\; Hg_2Ac_2 - Hg \qquad (4a)$$

(Ac = Acetate) $\longleftrightarrow$ glass electrode

$$\text{(Pt) } H_2 \;\Big|\; \begin{matrix}\text{0.1M HAc}\\ \text{0.1M NaAc}\end{matrix} \;\Big|\; Hg_2Ac_2 - Hg \qquad (5a)$$

would be the same if the glass electrode shows the correct hydrogen ion response in acid X. The contribution of the glass electrode asymmetry potential to cell 4a is not considered, and in their papers[20,21] they give no indication of whether they regard the asymmetry potential as constant or variable. In fact, the asymmetry potential is not mentioned except from a purely theoretical standpoint. Also, although they point out in these publications, that an advantage of using hydrogen rather than saturated calomel as the reference electrode is that the e.m.f.

$$\text{(Pt) } H_2 \;\Big|\; \text{Solution} \;\Big|\; \text{glass electrode}$$

should be independent of the nature of the solution, it can be seen from Glockner's Dissertation[77] that the e.m.f. of cell 4a was not measured directly for solutions in which the glass electrode showed no error.

Instead the asymmetry potential was measured using the cell:

$$Hg - Hg_2Ac_2 \;\Big|\; \begin{matrix}\text{0.1M HAc}\\ \text{0.1M NaAc}\end{matrix} \;\Big|\; \text{glass} \;\Big|\; \begin{matrix}\text{0.1M HAc}\\ \text{0.1M NaAc}\end{matrix} \;\Big|\; Hg_2Ac_2 - Hg \qquad (6a)$$

and E_{4a} was calculated using an observed value of E_{5a}. (In some cases the standard acetate buffer was saturated with sodium chloride and calomel

electrodes were used.) The electrode was then polarised to measure its resistance and after some unspecified time, was washed with water, dried with filter paper and placed in acid solution where its potential was measured against a hydrogen electrode. As they donoted the asymmetry potential by π_A and the error of the glass electrode by $\Delta\pi_A$, it appears that they regarded the error as a change of asymmetry potential, and assumed that the asymmetry potential was constant from the time when it was measured to the moment when the electrode was placed in the acid solution. This assumption was hardly justifiable even though their e.m.f's. were only measured to $\pm$0.4mV.

The only work with a precision comparable to the work in this department has been carried out by Zielen.[31] He compared his glass electrodes with hydrogen electrodes placed in the same solutions and used the transfer and extrapolation procedure to allow for changes of asymmetry potential. The glass and hydrogen electrodes occupied the same cell compartment and it appears that on transfer to a new cell the glass electrode was washed with solution that was not saturated with hydrogen. Thus when the glass electrode was placed in the cell the hydrogen electrode equilibrium would be disturbed and would require a few minutes to recover. Furthermore his cells did not contain any reference electrodes as a check on the hydrogen electrodes. However, in view of the fact that he obtained excellent agreement between the glass and the hydrogen electrodes, these shortcomings, particularly the second one, cannot be considered to be very serious.

5.4. Procedures used in the Present Work.

Experimental Procedure: In this work, the pH responsive glass electrodes were compared directly with hydrogen electrodes placed in the same solutions and the hydrogen electrodes in the different cells were connected to the measuring circuit by a common lead. The potential of each hydrogen electrode was checked with a suitable reference electrode reversible to an anion of the solution. Hence at no point in the cell was there a liquid junction with its attendant uncertainties. The hydrogen and reference electrodes were allowed to attain thermal and electrochemical equilibrium before glass electrode measurements commenced and as has been explained in section 4.1, the cells were designed so that these electrodes were not disturbed during glass electrode transfers. The hydrogen-reference electrode e.m.f's. were measured at 2 hour intervals, immediately after standardising the measuring circuit, and were then corrected to a hydrogen partial pressure of one atmosphere. The corrected e.m.f's. were constant to ±0.1mV for 8 or 9 hours and similar reproducibility was obtained between cells containing the same solution in different experimental runs.

Much the same procedure was used for testing cation responsive glass electrodes. The main difference was that the glass electrode potentials were now measured against silver-silver chloride electrodes and these were connected by a common lead instead of the hydrogen electrodes. The cells still contained hydrogen electrodes and the hydrogen - silver-silver chloride

e.m.f's. were again measured periodically but in this instance in order to check the correct functioning of the silver-silver chloride electrodes.

During an experimental run, up to six cells were placed one in front of another in the air thermostat. The centre compartments of the cells were closed with B 45 glass stoppers, when not containing a glass electrode. When a glass electrode was transferred between two cells, it was washed for ten seconds with the new solution using a polythene wash-bottle as recommended by Caudle.[1] The overall time between the last observed e.m.f. for the first solution and the first e.m.f. reading for the second, was usually not more than 30 seconds. The wash-bottles containing portions of the different cell solutions were also kept in the air thermostat. This procedure is undoubtedly preferable to washing an electrode with distilled water and drying it with filter paper as it causes less disturbance to the electrode.

When hydroxide solutions were used in an experimental run, it was necessary to exclude atmospheric carbon dioxide both when setting up the cells and during transfers of the glass electrodes. If carbon dioxide were present it would contaminate the solutions and this might result in a difference in solution composition between the glass and hydrogen electrode compartments of the same cell. No more than two hydroxide solutions were included in any experimental run and the cells containing these solutions were set up, and the polythene wash-bottles filled, under nitrogen in the air thermostat. The cells were sealed and the thermostat door was then

opened to admit the other cells which had been set up on the laboratory bench. Later the thermostat was again filled with nitrogen when the glass electrodes were being tested in the hydroxide solutions.

pH of Solutions: Measurement of the hydrogen-reference electrode e.m.f. for a cell provided, in addition to a check on the correct functioning of the two electrodes, a measure of the pH of the cell solution. Many of the solutions used in the present work contained either chloride or bromide ions, and when presenting the glass electrode data, these solutions have been specified in terms of the p_wH, originally introduced by Bates,[78] and defined, in the case of a chloride solution for example, by:

$$p_wH = - \log a_{H+} \gamma_{Cl-}$$

where a_{H+} is the activity of the hydrogen ion and γ_{Cl-} is the activity coefficient of the chloride ion, both on the molality scale. Unlike the quantity pH defined as $pH = - \log a_{H+}$, p_wH is physically defined at all ionic strengths, and can be determined from the e.m.f. of a cell without liquid junction, composed of the solution in question and electrodes reversible to the hydrogen and halide ions. The most reproducible cell of this type involves the hydrogen and silver-silver halide electrodes as used in this work. The p_wH is computed using the expression:

$$p_wH = \frac{F(E - E_o)}{2.303RT} + \log m_{Cl-}$$

(again considering a chloride solution) where E is the cell e.m.f. with the

partial pressure of hydrogen equal to 1 atmosphere, E_o is the standard potential of the silver-silver chloride electrode and m_{Cl^-} the chloride ion molality. As indicated earlier, a given solution was normally used to set up cells in two of three experimental runs and the observed e.m.f's. did not differ by more than 0.2mV, when corrected to a hydrogen partial pressure of 1 atmosphere. The p_wH of a solution could therefore be calculated to the nearest 0.01 of a p_wH unit. Since glass electrodes are most frequently used to measure pH on the practical scale, the relationship between the p_wH and the pH measured on the practical scale will now be considered.

On the practical pH scale, an unknown pH (pH_x) is measured in terms of the pH value assigned to a standard buffer (pH_s) and the e.m.f's. of the following cells:

(Pt) H_2 (1 atm.)	solution pH_s	Sat.KCl	Hg_2Cl_2 - Hg (E_s)
(Pt) H_2 (1 atm.)	solution pH_x	Sat.KCl	Hg_2Cl_2 - Hg (E_x)

The unknown pH is obtained from the relation:

$$pH_x = pH_s + \frac{F(E_x - E_s)}{2.303RT}$$

The pH value obtained in this way using cells with hydrogen electrodes will be referred to here as the 'correct pH' but this of course does not mean that $pH_x = -\log a_{H^+(x)}$. In practise the hydrogen electrode is replaced by a glass electrode and the pH is read directly from the pH meter. Provided the glass electrode shows no error, the value of $(E_x - E_s)$ obtained using the

glass electrode will be the same as that for the cells with hydrogen electrodes.

The e.m.f's. of the two cells above are given by:

$$E_s = E_{Cal} \pm E_{js} - 2.303\frac{RT}{F} \text{ Log } a_{H^+(s)}$$

and

$$E_x = E_{Cal} \pm E_{jx} - 2.303\frac{RT}{F} \text{ log } a_{H^+(x)}$$

where E_{Cal} is the potential of the saturated calomel electrode, E_{js} and E_{jx} are the liquid junction potentials and $a_{H^+(s)}$ and $a_{H^+(x)}$ are the hydrogen ion activities in the respective cells.

$$- \log a_{H^+(x)} + \log a_{H^+(s)} = \frac{F(E_x - E_s)}{2.303RT} \pm \frac{F\ \Delta E_j}{2.303RT}$$

where ΔE_j is the difference between the liquid junction potentials in the two cells. If the second term on the right hand side is small and can be neglected and if $- \log a_{H^+(s)} = pH_s$ then $- \log a_{H^+(x)} = pH_x$. If the solution of pH_x contains chloride ions then:

$$p_wH = - \log a_{H^+(x)} - \log \gamma_{Cl^-}$$

and

$$pH_x = p_wH + \log \gamma_{Cl^-}$$

pH_x may be estimated therefore, if it is assumed that γ_{Cl^-} is equal to the mean ionic activity coefficient of the chloride solution in question, and some examples will now be considered.

For a buffer solution without added salt, which contains simply an organic base, such as tris or ethanolamine and its hydrochloride or

hydrobromide, the mean ionic activity coefficient of the hydrochloride or hydrobromide is required. This could be obtained from the e.m.f. data of the present work in the following manner. The dissociation constant for the cation of the base is given by:

$$K_a = \frac{a_{H^+}\, a_B}{a_{BH^+}}$$

where the subscripts B and BH^+ refer to the free base and the undissociated cation respectively. Hence taking logarithms:

$$pK_a = pH - \log \frac{a_B}{a_{BH^+}}$$

Introducing molalities and activity coefficients, and rearranging the equation:

$$pH = pK_a + \log \frac{m_B}{m_{BH^+}} + \log \frac{\gamma_B}{\gamma_{BH^+}}$$

It is convenient now to define a quantity pH' given by:

$$pH' = pK_a + \log \frac{m_B}{m_{BH^+}}$$

which can be calculated from the known dissociation constant[61,79] and the molalities of the base and its cation which are determined when the solution is prepared. It follows that:

$$pH = pH' + \log \frac{\gamma_B}{\gamma_{BH^+}}$$

Substituting in the equation:

$$p_wH = pH - \log \gamma_{Cl^-}$$

one obtains: $$p_wH = pH' + \log \gamma_B - \log \gamma_{BH^+} \gamma_{Cl^-}$$

$$= pH' + \log \gamma_B - 2 \log \gamma_{\pm BHCl}$$

where $\gamma_{\pm BHCl}$ is the mean ionic activity coefficient of the hydrochloride. Since the undissociated base is a non electrolyte γ_B may be taken to be unity and hence $\log \gamma_B = 0$

$$\log \gamma_{\pm BHCl} = \tfrac{1}{2}(pH' - p_wH)$$

It was found that within the precision of the experimental data (±0.01 pH) the value obtained for $\log \gamma_{\pm BHCl}$ was determined only by the hydrochloride molality or ionic strength of the solution. It was found to be independent of the concentration of undissociated base and hence the pH of the buffer. It was also independent of the nature of the base at the two hydrochloride concentrations (0.1m and 0.5m) investigated, being the same for both tris and ethanolamine. This is to be expected if the activity coefficient of the free base is unity. The values obtained are given below:

Hydrochloride Molality	$pH' - p_wH$	$\log \gamma_{\pm BHCl}$	$\gamma_{\pm BHCl}$
0.1	-0.24 ± 0.01	-0.12 ± 0.005	0.76
0.5	-0.41 ± 0.01	-0.205 ± 0.005	0.62

The value of $(pH' - p_wH)$ for 0.1m hydrochloride agrees well with the value -0.239 obtained from the data of Bates[80] for a tris buffer of p_wH 8.321.

For ethanolamine buffers containing 0.1m bromide instead of chloride for the anion, the value of the mean ionic activity coefficient of the hydrobromide was the same, within the precision of the experimental method, as that for $\gamma_{\pm BHCl}$ at the same molality. Hence for these solutions the pH on the practical scale can be estimated from the expressions:

1. 0.1m Cl^- or Br^- $\quad pH_x = p_wH - 0.12$

2. 0.5m Cl^- $\quad pH_x = p_wH - 0.21$

Many of the solutions used in this work were tris and ethanolamine buffers with added salts. If the salt was not a halide then the activity coefficient of the halide in the solution might again be regarded as equal to the mean ionic activity coefficient of the hydrohalide of the base. For example, some of the lithium solutions consisted of 0.5m lithium sulphate in an ethanolamine buffer with 0.1m hydrochloride, and the following data were obtained:

$pH' - p_wH$	$\log \gamma_{\pm BHCl}$	$\gamma_{\pm BHCl}$
-0.58 ± 0.01	-0.29 ± 0.005	0.51

Hence for these solutions the pH on the practical scale can be estimated by the relation:

$$pH = p_wH - 0.29$$

The majority of the solutions used in this work, however, contained an alkali metal halide as the principal solute. Two procedures have been used for estimating the halide ion activity coefficient for these solutions. If activity coefficient data was available for the mixed electrolyte, the

activity coefficient of the halide ion was regarded as equal to the mean ionic activity coefficient of the halide in the mixture. Otherwise it was assumed that the activity coefficient of the halide ion was equal to the mean ionic activity coefficient of the alkali metal halide, when present in solution alone at the same ionic strength. Using the latter procedure the activity coefficient values were based upon the data of Robinson and Stokes.[55]

Both the above procedures were used when dealing with sodium chloride solutions and they, in fact, yielded essentially the same result. Activity coefficients of NaCl in NaOH - NaCl mixtures have been determined by Harned and Cook,[81] and for solutions of constant total molality of 1.0m can be expressed by the equation:

$$- \log \gamma_2 = - \log \gamma_{2(0)} + 0.029 m_1 - 0.020 m_1^2$$

where γ_2 is the activity coefficient of NaCl in the mixture, $\gamma_{2(0)}$ that in pure NaCl solution of the same total molality and m_1 the molality of NaOH in the mixture. The following values were calculated for the solutions used in the present work:

m_1 (NaOH)	m_2 (NaCl)	log γ_2	γ_2
0.10	0.90	-0.184	0.654
0.01	0.99	-0.182	0.658

$\gamma_{2(0)}$ (1.0m NaCl) = 0.658

For the following solutions, each of which contains NaCl as the major solute and has sodium as the only cation:

0.1m CH_3COOH + 0.1m CH_3COONa + 0.9m NaCl

0.05m $Na_2B_4O_7$ + 0.9m NaCl

then pH on the practical scale was estimated using the value of $\gamma_{\pm NaCl}$ at 1.0m given by Robinson and Stokes:

$$\gamma_{Cl^-} = \gamma_{\pm NaCl} = 0.657$$

$$\log \gamma_{Cl^-} = -0.182$$

For the following solutions:

1.0m NaCl + 0.1m $(CH_2OH)_3CNH_3Cl$ + $(CH_2OH)_3CNH_2$ (Tris buffer)

1.0m NaCl + 0.1m $(CH_2OH)_3CNH_3Cl$ + $(CH_2OH)_3CNH_2$ (Ethanolamine buffer)

the chloride ion is the only anion present, and for these, the activity coefficient of the chloride ion was assumed to be equal to $\gamma_{\pm NaCl}$ at 1.1m.

$$\gamma_{Cl^-} = \gamma_{\pm NaCl} = 0.655$$

$$\log \gamma_{Cl^-} = -0.184$$

Hence for all these sodium solutions, the pH on the practical scale may be estimated using the relation

$$pH = p_wH - 0.18$$

This procedure has also been used for the following 1.0m potassium solutions buffered with ethanolamine:

1.0m KCl + 0.1m $(C_2H_4OH)NH_3Cl$ + $(C_2H_4OH)NH_2$

1.0m KBr + 0.1m $(C_2H_4OH)NH_3Br$ + $(C_2H_4OH)NH_2$

Again the data of Robinson and Stokes was used and the following relationships

were obtained:

$$KCl \qquad pH = p_wH - 0.22$$

$$KBr \qquad pH = p_wH - 0.21$$

From these calculations it can be seen that for the purposes of the present work, the difference between p_wH and the pH on the practical scale is small. Hence although p_wH was actually measured in this work the term pH will be used when discussing the results unless it is necessary to refer to p_wH specifically.

Analysis of Glass Electrode Data: As was mentioned in section 5.2, rapid changes of e.m.f. known as transients were frequently observed immediately after a glass electrode was transferred to a new solution. These transients were characterised by an initially large $\left|\frac{d^2E}{dt^2}\right|$, where E is the e.m.f. of a cell:

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Solution} \ \Big|\ \text{glass electrode}$$

and t is the time. $\left|\frac{d^2E}{dt^2}\right|$ became zero or very small as the transient died away and extrapolation back to the instant of transfer was not possible. $\left|\frac{dE}{dt}\right|$ was usually initially large also and its final almost constant value was small or zero. The e.m.f.- time plots also featured a much less rapid type of change (i.e. $\left|\frac{d^2E}{dt^2}\right|$ and $\left|\frac{dE}{dt}\right|$ were both small or zero) which will be termed a drift of e.m.f. When this type of variation was observed immediately after an electrode was transferred to a new solution, extrapolation to the instant of transfer was possible within the precision of the experimental

method (± 0.2mV). Some transients showed a turning point at which $\left|\frac{dE}{dt}\right|$ became zero at a time when $\left|\frac{d^2E}{dt^2}\right|$ was still large. If on the other hand a turning point occurred when $\left|\frac{d^2E}{dt^2}\right|$ had become practically zero, the plot could be described as a transient followed by a drift of e.m.f. Some examples of possible e.m.f. - time curves including those just mentioned, are shown in figure 4.

Since it has been found that a wide range of e.m.f. - time variations are possible for cells involving glass electrodes, it has proved useful to have a method of classifying their main features. Caudle[1] introduced such a classification and this has been used as a basis for dealing with the data obtained in the present work. However now that more experimental results have become available, it has been found desirable to extend, and in part to modify, the original classification. Caudle observed that the e.m.f. - time variations obtained with cells:

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Solution} \ \Big|\ \text{glass electrode}$$

may contain the following three features either singly or combined.

A. a rapid change over the first few minutes which is largely independent of solution composition and concentration and consequently is probably electrical rather than electrochemical in origin.

B. a zero, or slight and approximately linear change.

C. a rapid change, the rate of which slowly decreases.

Since the transients of response A are believed to be electrical rather than electrochemical in origin, Caudle termed them 'spurious transients'. Not only

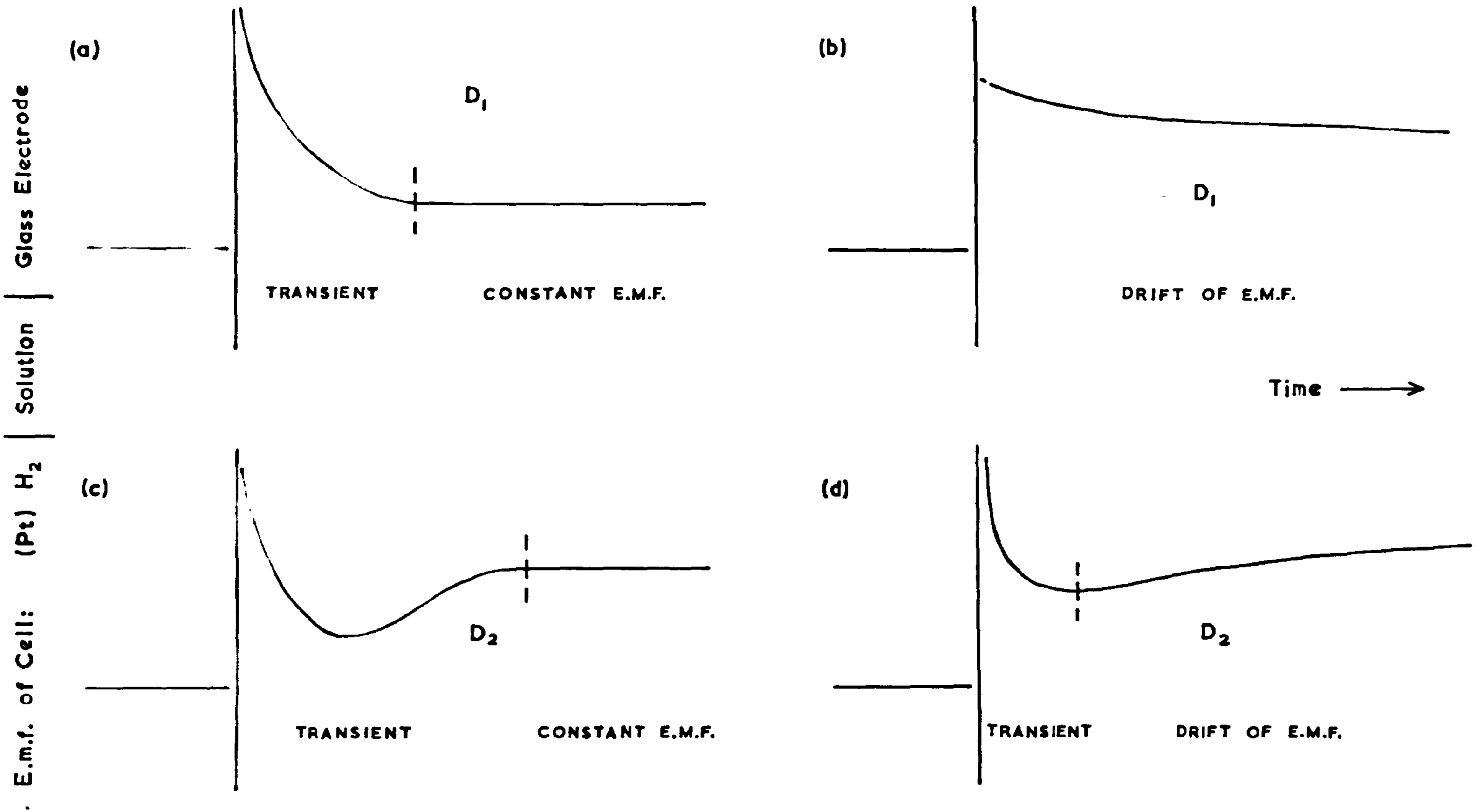


Fig. 4 Typical E.m.f.–Time Variations shown by Glass Electrode Cells.

are they independent of the nature of the cell solution but their magnitude and characteristics may be changed by varying the technique used for transferring a glass electrode from one cell to another. Caudle investigated these spurious transients and found that factors such as:-

a) the method and time of washing

b) use of gloves for holding the electrode

c) the size of the bung in which the electrode is mounted

d) waxing the electrode stem

e) switching of the electrical measuring circuit

influenced the nature of the transient which was observed. For example, he concluded that the transients were reduced if the glass electrodes were mounted in large bungs and the B45 size was chosen for this reason. He also found that transients of type A could be produced by procedures such as polarising the cell or electrostatic charging of the glass electrode surface. Response A can usually be identified in practice by observing that the transients are independent of the direction of transferring an electrode between two solutions, that is either random in direction or all in the same direction. Also the transients can be produced by carrying out the transfer procedure including washing the electrode without actually changing the solution.

As was observed earlier (chapter 2.3), Caudle found that some electrodes, i.e. those believed to have lithia glass membranes, gave a response of A + B in acid solutions and only at very high concentrations was A + C observed.

When feature A is followed by feature B the two parts of the e.m.f. - time curve are quite clear; however when feature A is followed by C it is often not possible to distinguish the two effects very clearly. When A + B response is observed, it is found that if the B portion of the e.m.f. - time curve is extrapolated to the instant of transfer neglecting the transient, feature A, the instantaneous error is small or zero whereas the initial e.m.f. actually indicates an error of perhaps 1-2mV. This is therefore an additional reason for regarding feature A to be electrical rather than electrochemical in origin. Examples of response A obtained in the present investigation will be discussed in the next chapter.

Discussion of feature B will be postponed and response of type C will now be considered. Caudle found that e.m.f. - time variations of type C could be subdivided into C_1 and C_2. With type C_1, the error was initially non-zero and increased with time at a slowly decreasing rate but C_2 was more complex and included turning points. It is apparent from Caudle's description of his results, that the type C_2 response which he observed, consisted of a transient with a turning point, followed by a drift of e.m.f. During the transient, the error, which was negative, first increased and then started to decrease and the drift of e.m.f. which followed corresponded to an increasing error. Hence the curve would have a second turning point at the beginning of the final slow drift.

In the present investigation a wider range of e.m.f. - time variations have been observed in connection with glass electrode errors, and it has been

found convenient to extend Caudle's original classification in this respect. The variations have been assigned to one of five types which have been designated C_1, C_2, D_1, D_2 and E, where only those of type E may invariably be extrapolated to the instant of transfer. Types C and D will be considered first. These are defined in terms of the error, which may be positive or negative, for the second solution relative to the first, irrespective of whether one of the solutions is a standard solution. Type C response (both C_1 and C_2) is characterised by an initial increase in the error and in type D response (both D_1 and D_2) the error is initially decreasing. With types C_1 and D_1 the variation of the error occurs at a decreasing rate and an approximately constant final value is observed. Types C_2 and D_2 both involve at least one turning point. Usually in this work, the e.m.f.-time variations of type C_2 and D_2 only contained one turning point and in the results chapters this may be assumed to be the case unless it is stated otherwise. These four types of response are illustrated in figure 5 for the case where an electrode shows a positive error in the second solution relative to the first. When the electrode gives a negative error in the second solution relative to the first, the transients are the mirror image about the abscissae of those shown in the figure.

The four types of response, C_1, C_2, D_1 and D_2, each include a wide range of possible types of glass electrode behaviour on account of the possible variation of the curvature of the e.m.f.-time graph. The types C_1 and D_1 range from a sharply curved transient which dies away to give a steady e.m.f.,

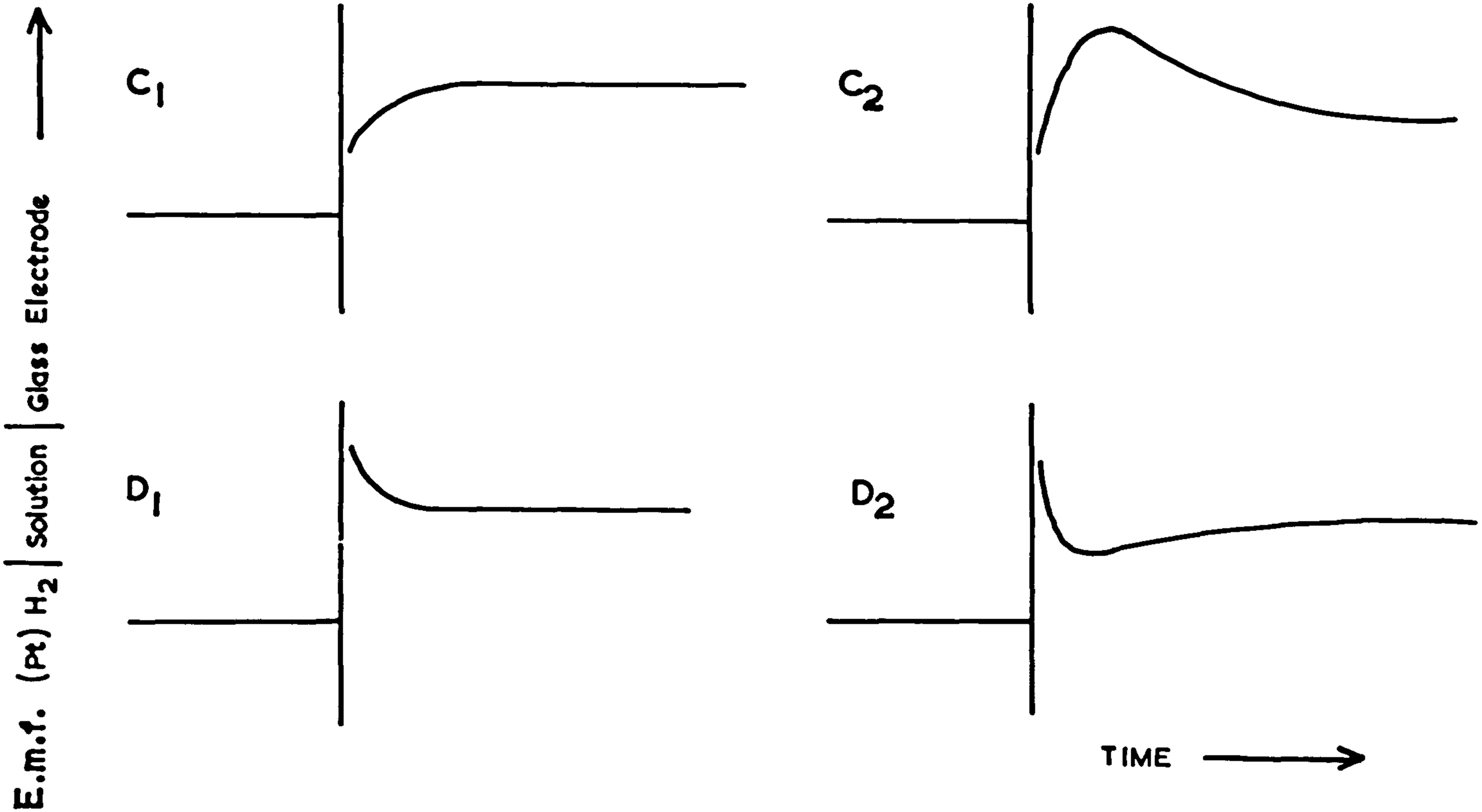


Fig. 5 CLASSIFICATION OF TIME-VARIATIONS SHOWN BY GLASS ELECTRODE ERRORS

to a slow drift of e.m.f. in which $\left|\frac{d^2E}{dt^2}\right|$ is small (Figure 4, a and b).

The general types of response C_2 and D_2 have been observed to vary from

1) a transient which changes direction followed by a constant e.m.f., to

2) a transient which does not change direction followed by a drift of e.m.f.

(Figure 4, c and d). It can be seen that D_1 response is a special form of C_2 in which the initial increase in error is not apparent. In fact, Caudle sometimes observed response of type D_1 when testing glass electrodes in acid solutions and considered it to be a form of type C_2. In the same way, the type of response C_1 is a form of D_2 in which the initial decrease in error is not observed.

The four types of response described in the last two paragraphs were specified in terms of the variation of the glass electrode error. However the definition of an error as given earlier is only applicable to the special case where the glass electrode is being compared directly with an electrode responsive to the same ion as itself. The definition of an error will therefore now be modified to make the types of response as specified above more generally applicable. For the case where a glass electrode is transferred between two cells containing reference electrodes reversible to the same ion as itself, the error at some time in the second solution was defined relative to the final e.m.f. for the first. If a different reference electrode, such as the silver-silver chloride electrode, is being used the error must be defined in terms of the e.m.f. which the second cell should have immediately after transfer of the glass electrode. This e.m.f. can be calculated from the

final e.m.f. for the first cell and the theoretical e.m.f. difference. This is illustrated in figure 6 for the case of D_1 response in the second cell. The theoretical e.m.f. difference is denoted by E_{Th}. It can be seen that it would be unrealistic as well as difficult to define the transient for the positive error in figure 6 relative to the final e.m.f. in the first cell, since the error defined in this way changes sign. In the special case where reference electrodes responsive to the same ion as the glass electrode are used, the correct e.m.f. for the second cell immediately after transferring the glass electrode, is the same as the final e.m.f. for the first cell.

Response of Type E may be defined on similar lines to type B, i.e. a zero, or slight and approximately linear change. However although it has not been specifically stated,[1,2] type B has usually been thought of in the past as being associated with the observation of the true pH response. An e.m.f. variation of this type will therefore be redefined as one which, when extrapolated back to the instant of transfer, indicates negligible instantaneous error, considering the performance precision of the glass electrode in question. An e.m.f. - time variation of type E indicates an error of the pH response of the electrode on extrapolation to the instant of-transfer. As will be seen later the extrapolation procedure is theoretically meaningless when an electrode shows an error, and for this reason these two types of e.m.f. - time variation, although similar, have been called B and E rather than B_1 and B_2. However, the extrapolation of response E might prove to be a useful procedure from the purely practical standpoint. For

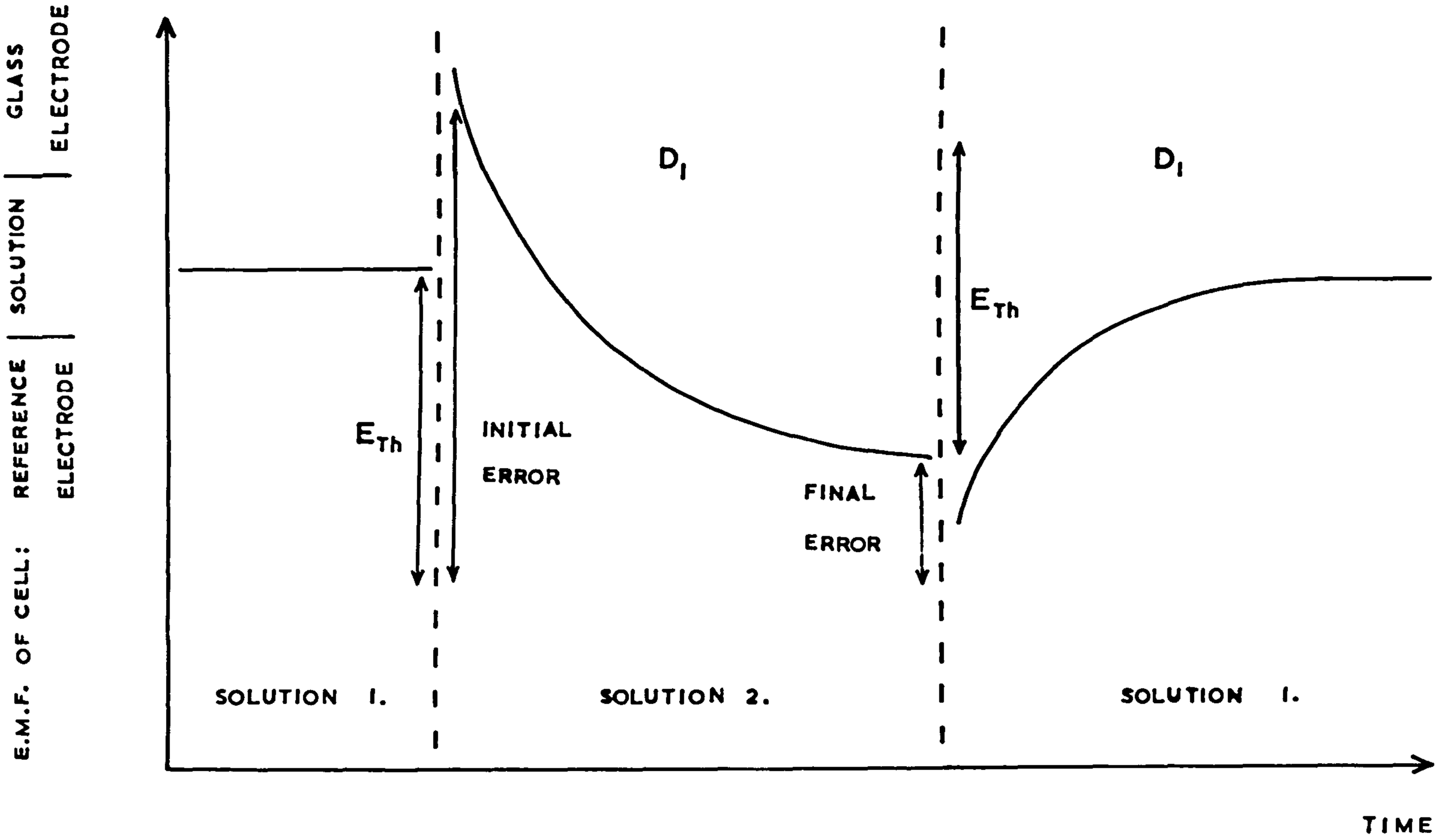


Fig. 6 REVISED DESCRIPTION OF GLASS ELECTRODE ERRORS

example, it might be found that the instantaneous error was more reproducible than the error at any later time.

It may be argued that response of type C or D may end with "a zero, or slight and approximately linear change". However while this may be true, often the transient part of the e.m.f. - time variation is large and dies away so slowly that it is impossible to say with certainty where the transient part of the curve ends and the drift of e.m.f. begins. Furthermore it would obviously not be possible to extrapolate this drift of e.m.f. back to the instant of transfer. Hence the definitions of response of types B and E will be further modified to indicate that the drift of e.m.f. must be observed sufficiently soon after transfer of the glass electrode to permit extrapolation to the instant of transfer. Response B will therefore be defined as a zero or slight and approximately linear change, observed to begin within about three minutes after transferring an electrode to a new solution, which may be extrapolated to give zero or negligible instantaneous error. Response E will be defined as a zero, or slight and approximately linear change observed to begin within about three minutes after transferring an electrode to a new solution, which may also be extrapolated to the instant of transfer but indicates an error in the pH response of the electrode. Hence if an e.m.f. - time curve for a glass electrode is described as A + B, C + E or D + E, it means that the transient part of the curve did not last more than about three minutes.

The procedure which Caudle termed 'stepwise transfers' has been used

frequently in the present work. A glass electrode is placed in a standard solution and the drift of e.m.f. observed for a suitable period (5-10 minutes). Then the electrode is transferred to a test solution and the e.m.f. - time variation is again followed, usually until an approximately constant value has been attained. The electrode is then transferred back to a standard solution. The standard solution in which the electrode is placed initially will be called standard solution 1. and that to which the electrode is transferred from the test solution will be called standard solution 2. The two standard solutions may of course be the same and it will be seen that for many tests this was the case.

When a glass electrode was tested in a solution where it was found to show a deviation from its pH response, transients were often observed, both immediately after the electrode was transferred to the test solution and after it was transferred back to a standard solution. Both for the test solution and for the standard solution these transients were usually followed by an approximately constant final e.m.f. Since the transients made it impossible to extrapolate the e.m.f. - time curves back to the times of transfer, the error of the glass electrode in the test solution was calculated from the approximately constant final e.m.f. (E_3) for the test solution

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Test Solution} \ \Big|\ \text{glass electrode} \qquad (3)$$

and the values for the calibration e.m.f. (E_7)

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Standard Solution} \ \Big|\ \text{glass electrode} \qquad (7)$$

observed immediately before transfer of the glass electrode to the test

solution and following the transient after transfer from the test solution. The precision with which the error can be quoted depends upon the constancy of the final e.m.f. for the test solution and the overall reproducibility of E_7. If the asymmetry potential has remained constant for the duration of the test, E_7 will have the same value for standard solution 1 and after the transient for standard solution 2. If this has not been the case then the variation of E_7 contributes to the uncertainty in the error for the test solution. The type of result which might be obtained is shown in figure 7a. If the overall variation of asymmetry potential is given by $2\delta E_7$ and the uncertainty in the final e.m.f. for the test cell is $\pm\delta E_3$ then the glass electrode error in the test solution is given by

$$\Delta E = E_3 - E_7 \pm (\delta E_3 + \delta E_7)$$

Unless otherwise stated, the above procedure has been used in calculating the magnitudes of the errors tabulated in the results chapters and usually the values may be regarded as correct to 0.01 of a pH unit that is having an accuracy of ±0.3mV. However in a few cases it has seemed reasonable to regard part of the e.m.f.-time variation in the test solution as a change of asymmetry potential. Before discussing this modification, the significance of the asymmetry potential when a glass electrode shows a deviation from its pH response, will be considered.

Following the hypothesis of Beck and Wynne-Jones,[28] it seems probable that the processes which take place at the surface of a glass electrode may be broadly divided into two types, electrochemical and chemical. The

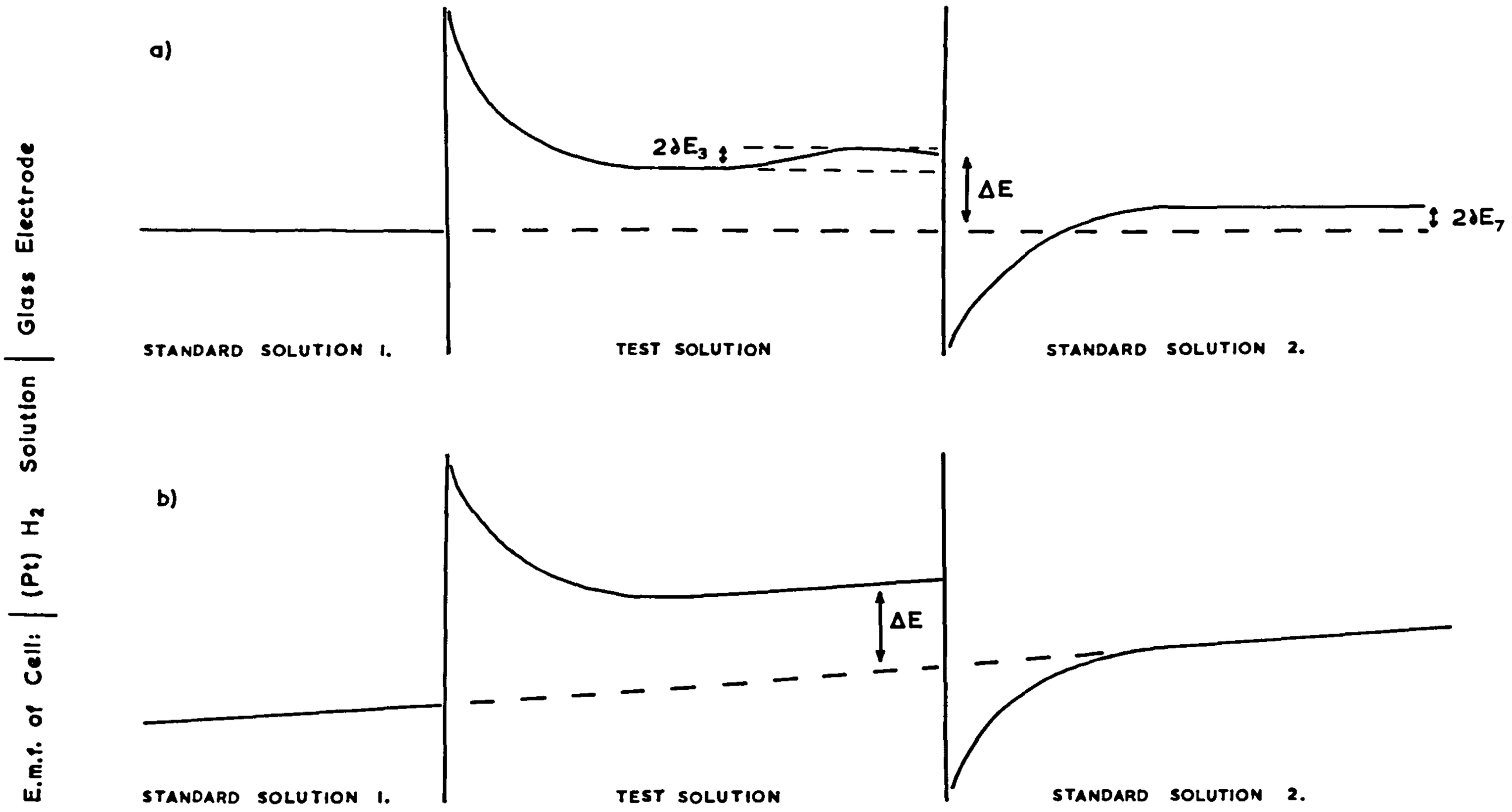


Fig. 7 Determination of Glass Electrode Errors (pH Response).

electrochemical processes involve a charge transfer across the glass-solution interface and in solutions where the electrode shows a theoretical response to a specific ion only one such process will be taking place. In the case of a pH responsive electrode in a standard solution, for example, the electrochemical process will be a transfer of hydrogen ions between the glass and the solution. The chemical processes do not involve a charge transfer and only affect the electrode potential in so far as they influence the chemical potentials of the species in the surface layer of the glass. These processes may include ion exchange or the adsorption or desorption of solvent and other neutral molecules. The asymmetry potential is thought of as arising from the differences in the chemical potentials of the ions in the surface layers on the two sides of the glass membrane and variations of asymmetry potential are regarded as being due to the chemical processes listed above. The two main types of process outlined above may of course be related since ions which take part in the electrochemical reactions may also be involved in the ion exchange process.

When a glass electrode shows a deviation from its pH response it is almost certain that ions other than hydrogen ions enter the glass surface and the error, therefore, is in part a change of asymmetry potential, since one surface of the glass membrane is being changed relative to the other. The concept, of the asymmetry potential of a glass electrode being the same in two cells at the instant of transferring the electrode between them, is therefore unlikely to be valid when the electrode shows a deviation from its

pH response. Hence the asymmetry potential (defined for the same solution on both sides of the glass membrane) for the electrode in a test solution is the hypothetical e.m.f. of cell 6 (page 65);

$$\text{Ag - AgCl} \;\big|\; \text{0.1m HCl} \;\big|\; \text{glass} \;\big|\; \text{0.1m HCl} \;\big|\; \text{AgCl - Ag} \qquad (6)$$

with the outer glass surface in the same state as in the test solution. That is to say with the chemical potentials of the species in the outer surface of the glass, the same as when the electrode was placed in the test solution. Thus when a glass electrode is placed in a solution in which it shows an error in its pH response, if the asymmetry potential is not considered to be constant it becomes inseparable from the change in the electrochemical process.

When testing a glass electrode by the stepwise transfer procedure described above, comparison of the e.m.f. E_7 observed for standard solution 2, after any transient has died away, with the value observed earlier for standard solution 1, shows whether or not there has been any overall change of asymmetry potential. If a change has occurred it may have resulted from a process or processes independent of the nature of the solution in contact with the outer surface of the glass membrane. It might, for example, have been due to a 'chemical' process taking place slowly at the inner surface, or a slow change, such as desorption or adsorption of water, at the outer surface of the glass, which is independent of the nature of the outer solution. Alternatively this overall change in asymmetry potential may have been caused by the test solution itself or a combination of both possibilities.

If the drift of e.m.f. observed for standard solution 2, after any transient, is a continuation of (i.e. collinear with) the drift of e.m.f. previously observed for standard solution 1, it would seem that the asymmetry potential change has been due to the first possibility. This is illustrated in figure 7 b. In such a case it would appear reasonable to consider the error in the test solution relative to the dotted line rather than the average of the values of E_7 for the two standard solutions as indicated earlier. In this way the contribution to the e.m.f. - time variation for the test solution made by processes which are independent of this solution is probably eliminated. During some experiments, changes of asymmetry potential have been observed, which have apparently been due to contact of the outer glass surface with the test solution in question and these will be referred to in the results chapters.

CHAPTER 6

Principle Features of Results for pH Responsive Electrodes.

6.1. The Response in Standard Solutions

Caudle[1] has shown that under suitable conditions glass electrodes may agree with the hydrogen electrode to ±0.3mV and in some cases to ±0.1mV. However his work and the two other similar investigations[30,31] have all been confined to acid solutions. Since the present work was mainly concerned with the response of glass electrodes in alkaline solutions, it was important to ascertain first of all whether the electrodes agreed with the hydrogen electrode to the same level of precision, when transferred between solutions of widely different pH. Furthermore if standard solutions in the alkaline pH range could be found, it would then be of interest to determine whether the response of a glass electrode in a solution where it gave an error, was influenced by the pH of the standard solution from which it was transferred. For example, it was thought that it might prove to be preferable to test electrodes in alkaline solutions using a standard solution of similar pH, rather than an acid solution, since in this way the electrodes would only be subjected to a relatively small pH change when transferred to a test solution.

When testing glass electrodes in acid solutions, Caudle used 1m. H_2SO_4 as a standard solution "in an attempt to standardise the surface of the electrode chemically" and in this investigation it was thought initially

that it might be desirable to find a similar standard solution in the alkaline pH range. It was thought that an alkaline standard solution would have to be free of the small metal cations which are believed to cause the alkaline errors. Previous measurements with glass electrodes in this type of solution have been limited to tetra-alkylammonium hydroxides[4,13,16] and ammonia buffers[27] and have been insufficiently accurate for the purposes of the present work. It was therefore decided to examine the suitability of tris (pK_a 8.075)[79] or ethanolamine (pK_a 9.498)[61] as standard solutions, since it was thought unlikely that the large organic cations would be able to penetrate the glass surface. The bases have the advantages of being much less volatile than ammonia and more readily purified than the tetra-alkylammonium hydroxides. The different types of glass electrode were therefore tested in tris and ethanolamine buffers with a hydrochloride or hydrobromide concentration of 0.5m or 0.1m covering the pH range 7.1 - 10.5. Sulphuric acid, either 0.1m or 1m was used as a standard solution and stepwise transfers to and from the buffer solutions were carried out. Solutions of hydrochloric and hydrobromic acids were also included in some of the experiments.

Typical examples of the results are presented in tables 6.1 to 6.7 and figures 8 to 20. Some of the results have been presented graphically since it was not always possible to show clearly the various type A transients using tables. In tables 6.1 to 6.7 and in all other tables, for convenience when tabulating the data, the zero of time was taken as the moment of making the first e.m.f. measurement rather than the actual instant of transfer. However

TABLES 6.1 to 6.7 and 6.9 to 6.17

Values of e.m.f's. (E_7):

(Pt) H_2 (p) | standard solution | glass electrode

in volts.

The values designated ΔE on these tables are the small "instantaneous errors" as defined in section 5.2.

The following procedures used for these tables also apply to similar tables in later chapters and in the appendix.

1. Solutions are given in the order of testing for the glass electrode.

2. Abbreviations:

(i) 0.1mCl^-/T	Tris buffer with 0.1m tris hydrochloride
(ii) 0.1mBr^-/E	Ethanolamine buffer with 0.1m ethanolamine hydrobromide
(iii) Acetate, 1.0m Na^+	0.1m acetic acid + 0.1m sodium acetate + 0.9m sodium chloride

3. A figure in brackets below an e.m.f. value is the time (min.) at which this value was observed.

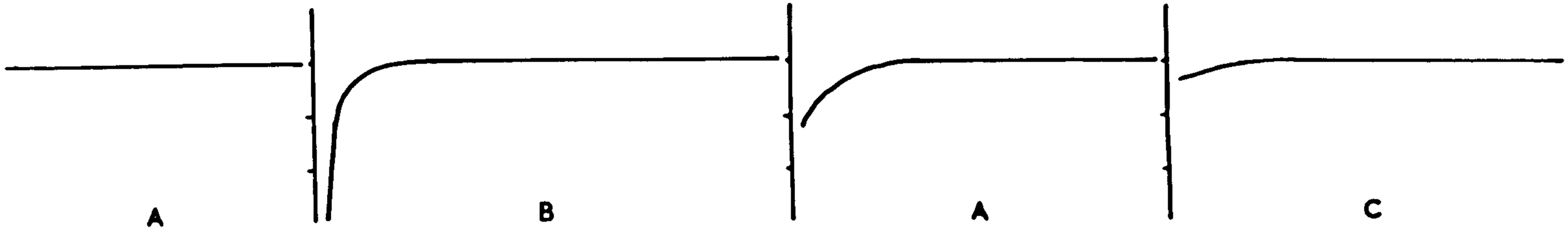
   The figure in brackets below a "final" e.m.f. value is thus the total time for which the electrode was placed in the solution.

FIGURES 8 to 20

Graphs of E_7 against time.

A vertical line represents the points at which the glass electrode was transferred between two cells.

1.



2.

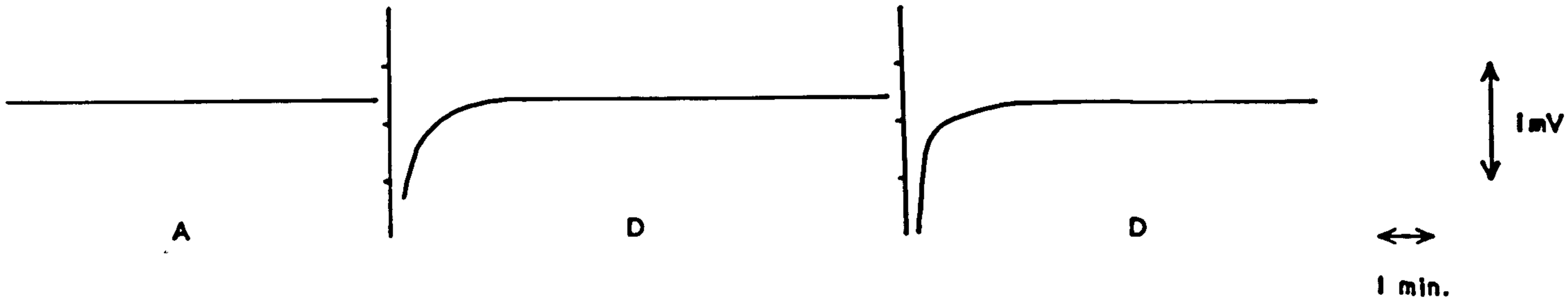


Fig. 8 1. ELECTRODE No. 22 (JENA HA)

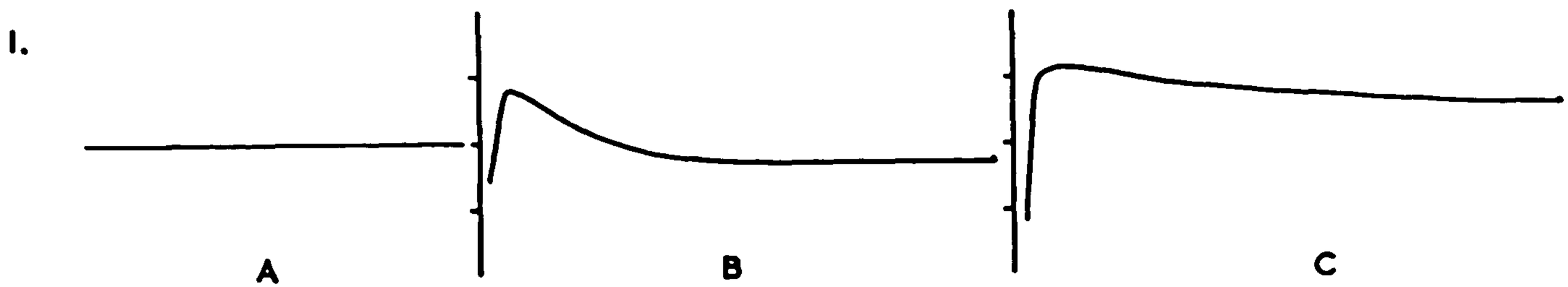
2. ELECTRODE No. 16 (RADIOMETER C)

A 0·1m H_2SO_4

B 0·5m HCl

C 0·1m Cl^-/ Ethanolamine

D 1·0m H_2SO_4



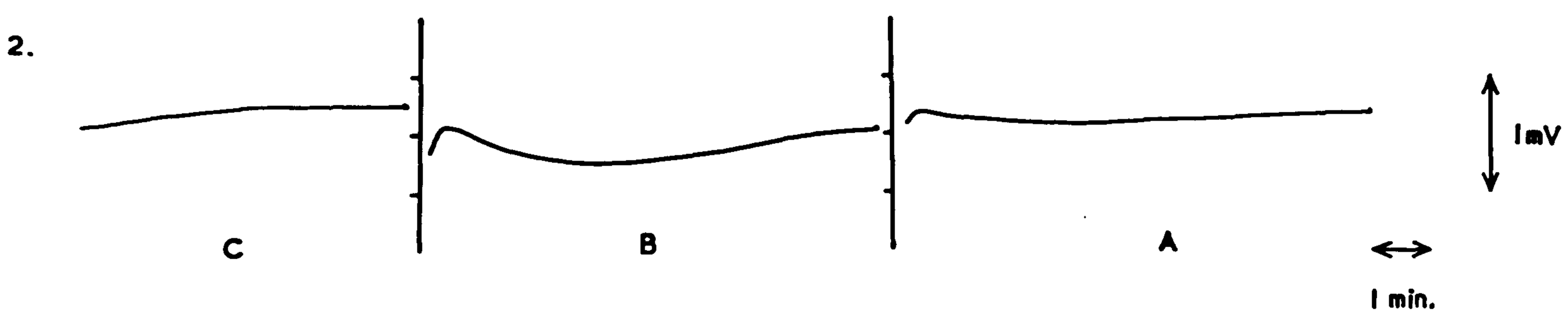


Fig. 9 ELECTRODE No. 19 (BECKMAN E2)

A 1·0 m H_2SO_4

B 0·1 m H_2SO_4

C 0·1 m Cl^- / Ethanolamine

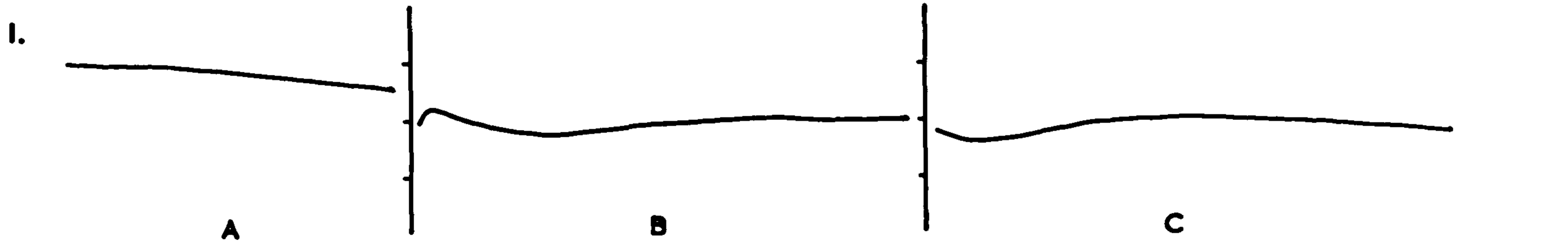
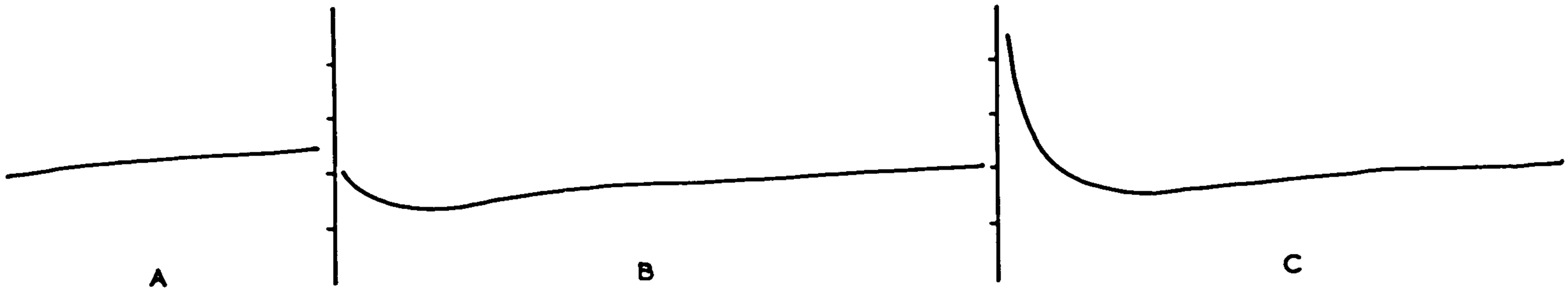


Fig. 10 ELECTRODE No. 15 (PYE INGOLD)

A 0·1m H_2SO_4

B 0·1m HCl

C 0·1m Cl^- / Ethanolamine



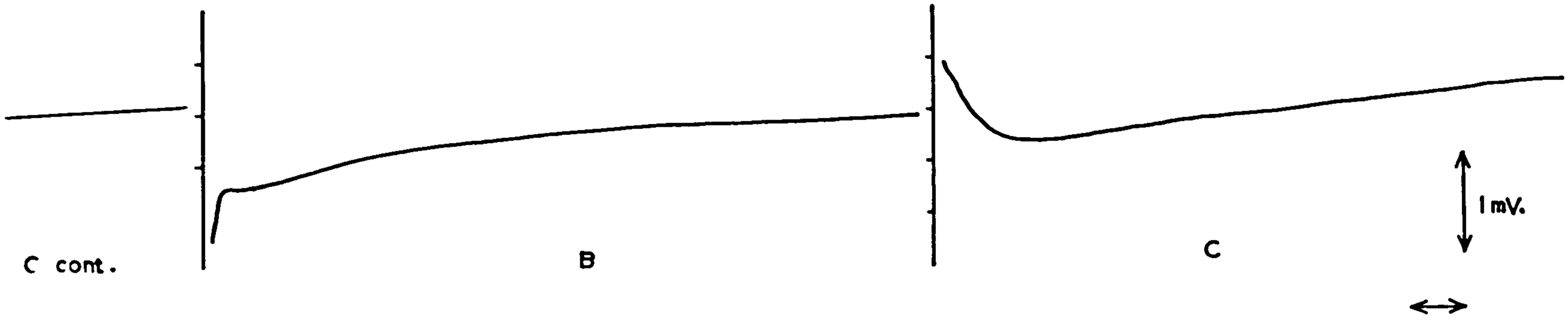


Fig. 11 ELECTRODE No. 18 (E.I.L. GHS 33)

A 1·0 m HCl

B 0·1 m H_2SO_4

C 0·1 m Cl^- / Ethanolamine + 1·0 m NaCl

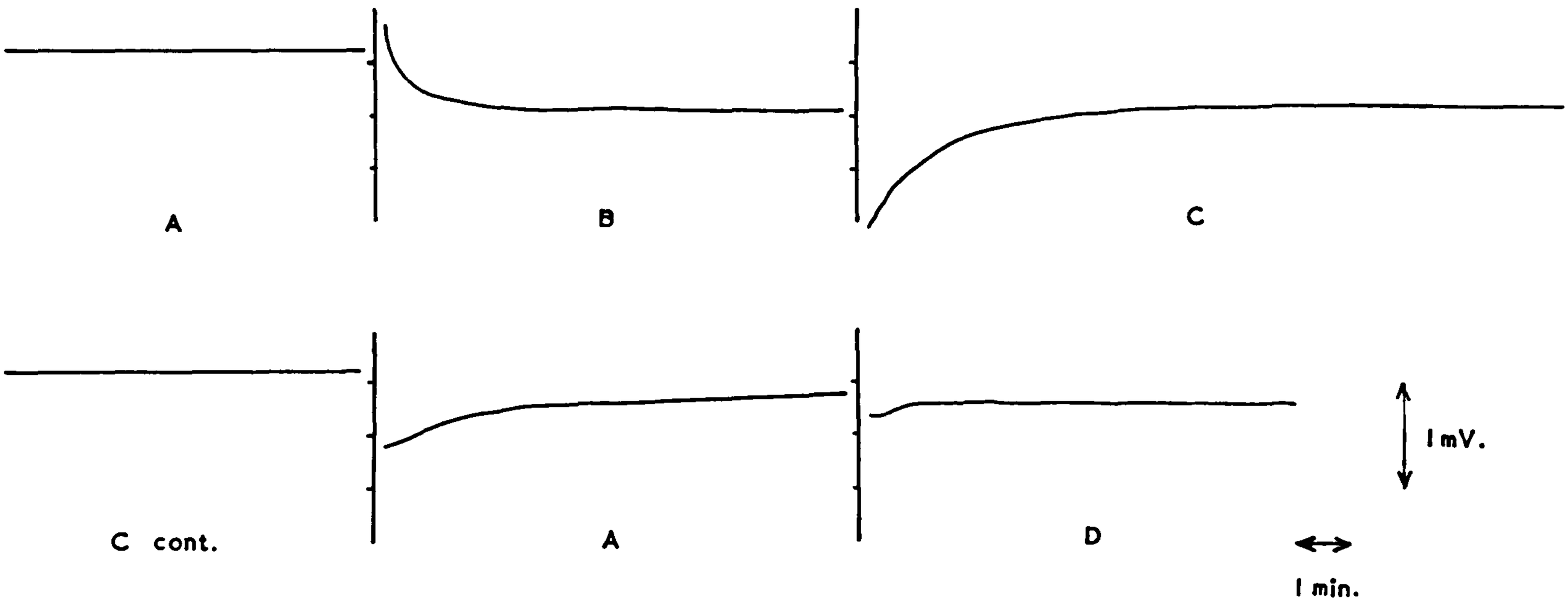


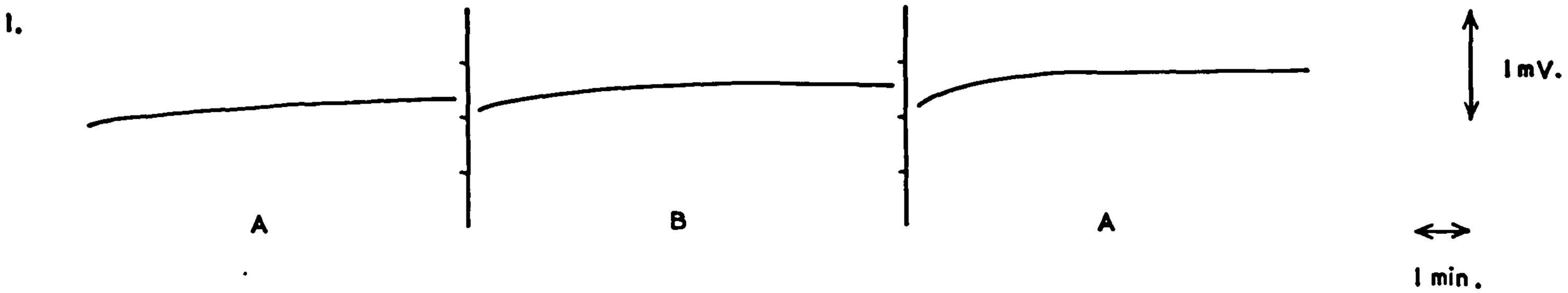
Fig. 12 ELECTRODE No. 11 (E.I.L. GHS 33)

A 0·1m H_2SO_4

B 0·1m Br^- / Ethanolamine

C 0·1m Cl^- / Ethanolamine

D 0·1m Cl^- / Ethanolamine + 1·0m KCl



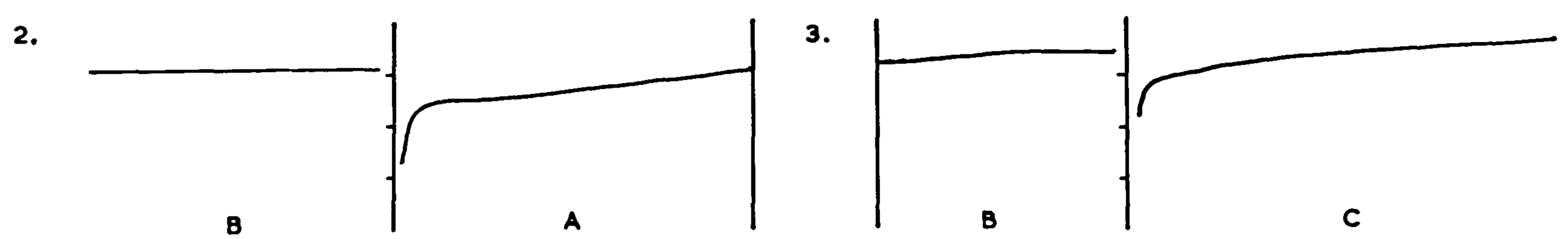


Fig. 13 ELECTRODE No. 15 (PYE INGOLD)

Stem Waxed.

A 0·1 m Cl^- / Ethanolamine

B 0·1 m H_2SO_4

C 1·0 m H_2SO_4

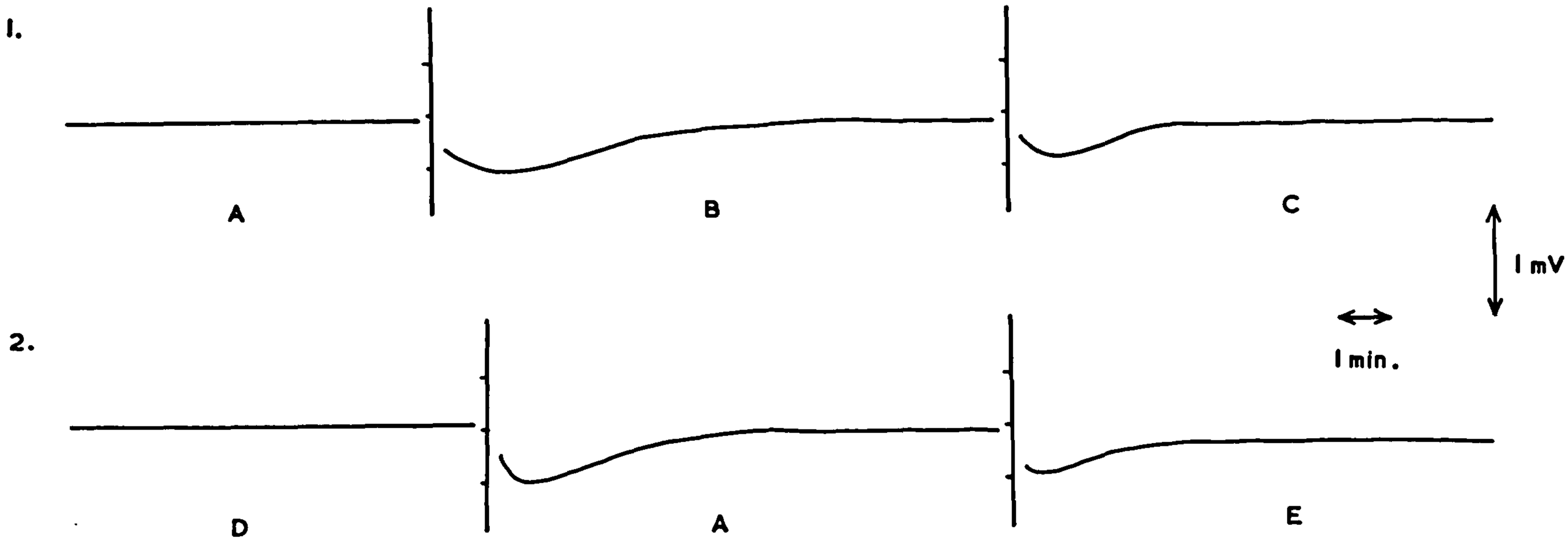


Fig. 14 ELECTRODE No. 14 (E.I.L GG 33)

A 1·0 m H_2SO_4

B 0·1 m HBr

C 0·1 m Br^- / Ethanolamine

D 0·1 m H_2SO_4

E 0·1 m Cl^- / Tris

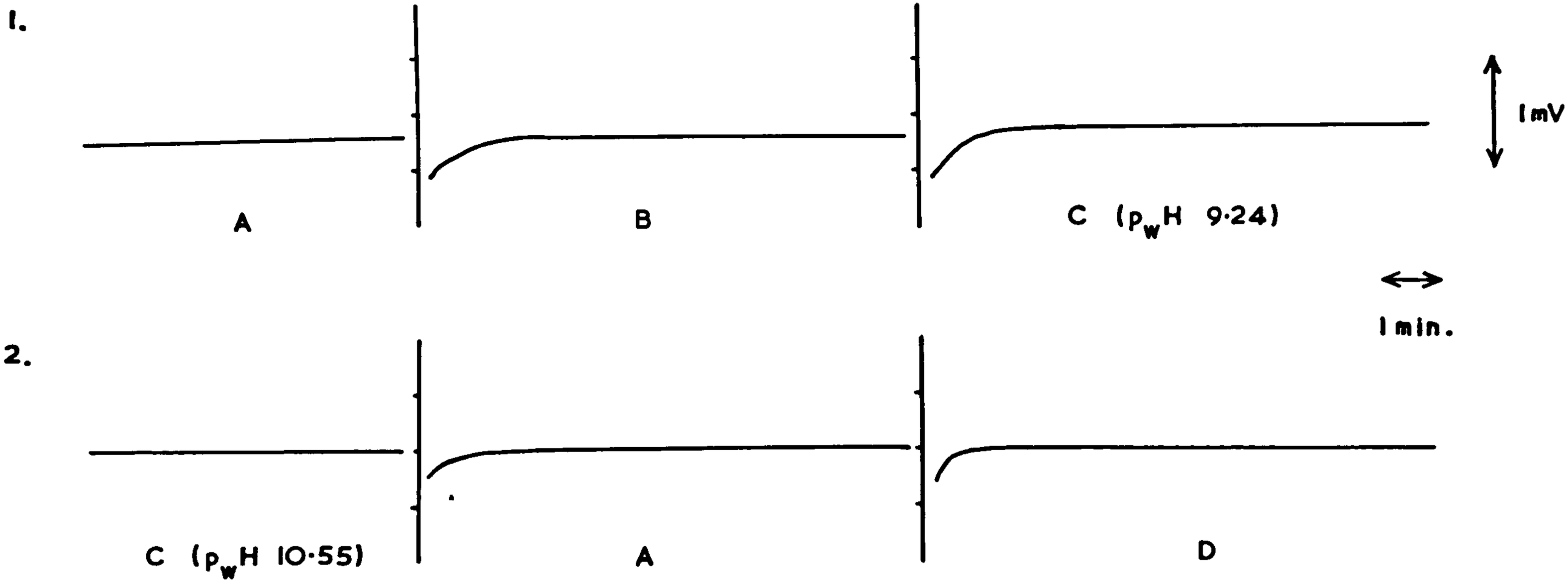


Fig. 15 ELECTRODE No. 14 (E.I.L. GG 33)

Stem Waxed.

A 0·1m H_2SO_4

B 0·1m Br^-/Ethanolamine

C 0·1m Cl^-/Ethanolamine

D 0·1m HBr

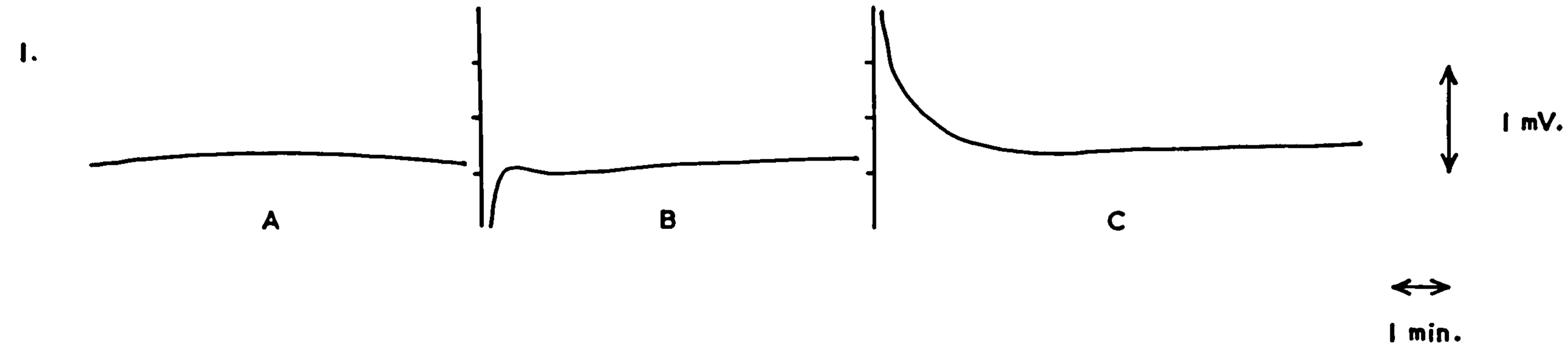


Fig. 16 ELECTRODE No. 19 (BECKMAN E2)

Stem Waxed.

A 0·1m H_2SO_4

B 0·1m Cl^- / Ethanolamire

C 0·1m Cl^- / Ethanolamine + 1·0 m NaCl

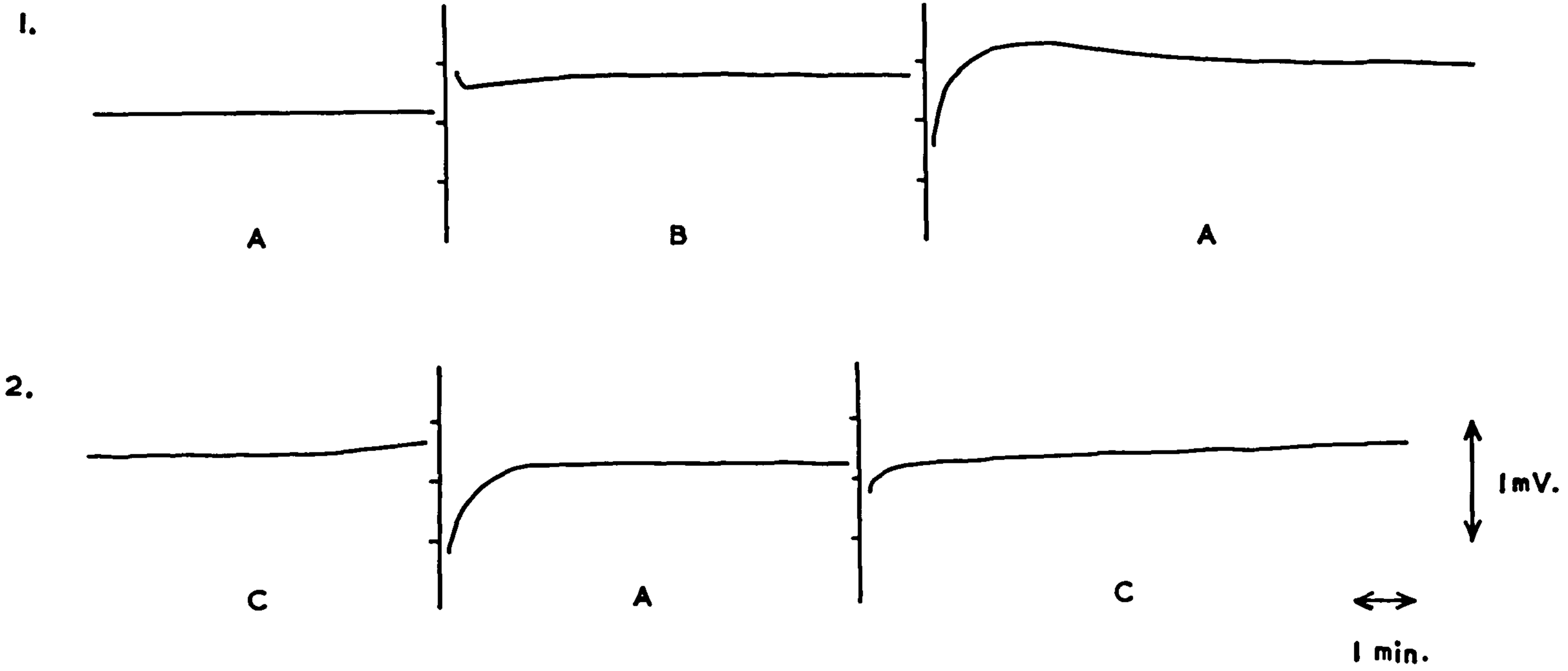


Fig. 17 ELECTRODE No. 18 (E.I.L. GHS 33)

Stem Waxed.

A 0·1m Cl^-/Ethanolamine

B 0·1m H_2SO_4

C 0·5m HCl

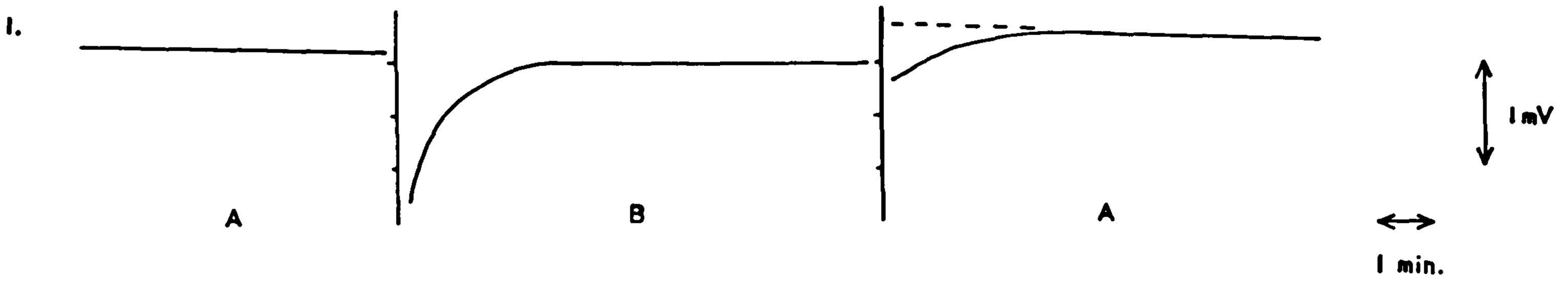


Fig. 18 ELECTRODE No. 11 (E.I.L. GHS 33)

Stem Waxed.

A 0·1m H_2SO_4

B 0·5m HCl

C 1·0m HCl

D 0·1m Cl^-/ Ethanolamine

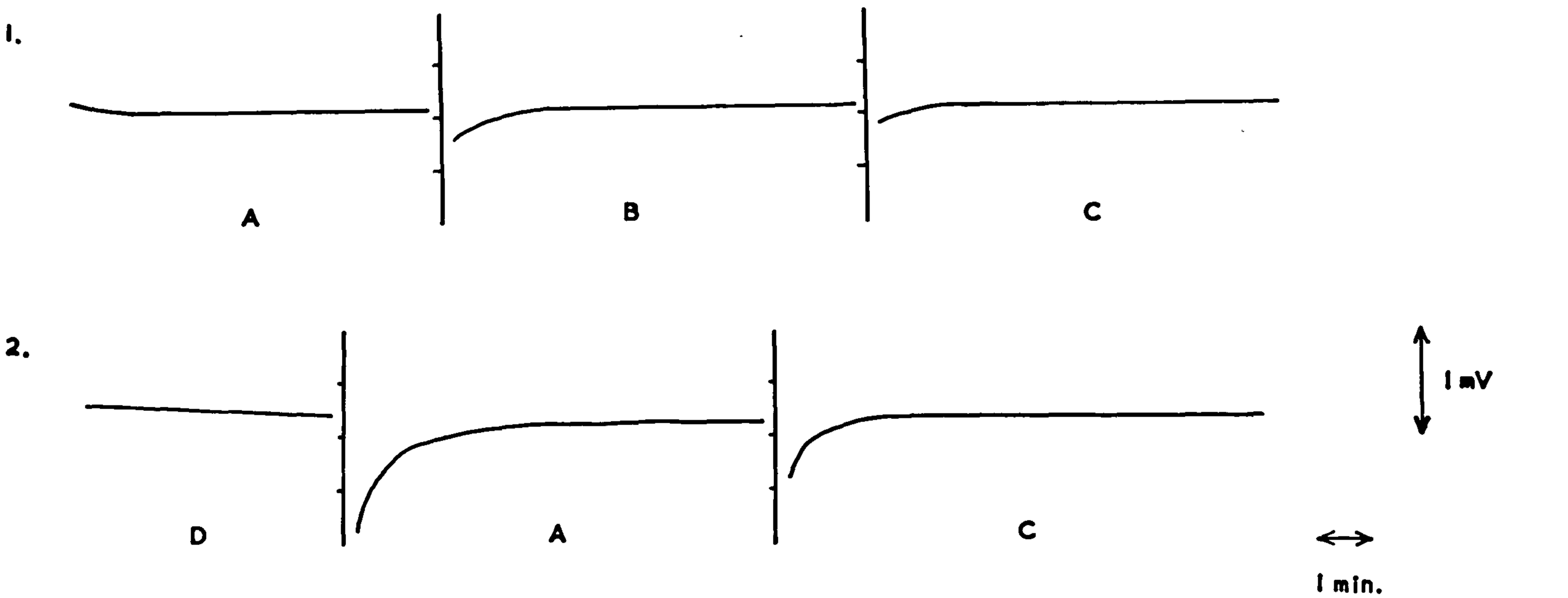


Fig. 19 ELECTRODE No. 17 (RADIOMETER B)

A 0·1 m H_2SO_4

B 0·1 m Cl^-/ Ethanolamine

C 0·1m Cl^- Ethanolamine + 1·0 m NaCl

D 1·0m HCl

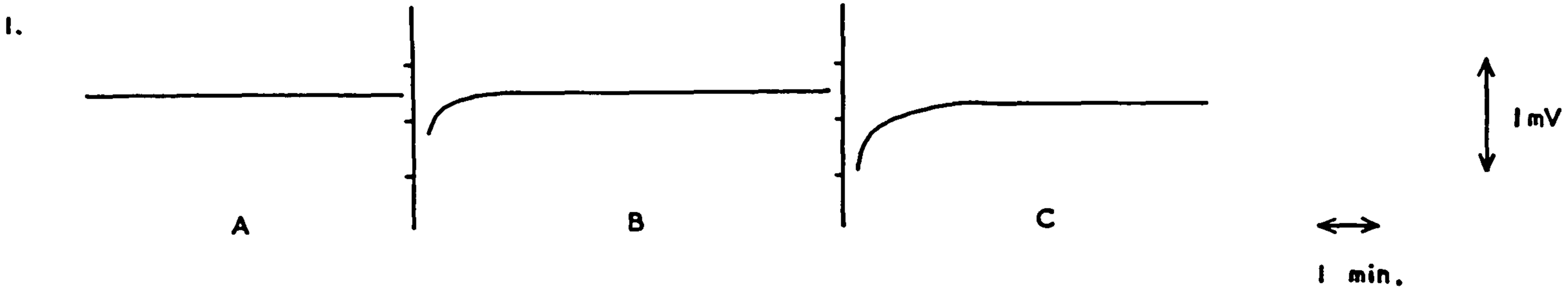


Fig. 20 ELECTRODE No. 17 (RADIOMETER B)

Stem Waxed.

A 0·05m $Na_2B_4O_7$ + 0·9m NaCl

B 0·1m Cl^-/Tris + 1·0m NaCl

C 0·1m H_2SO_4

D 1·0m H_2SO_4

E 0·1m Cl^-/Ethanolamine

TABLE 6.1.

Electrode No. 16.

10/8/65.

Initial Solution 1.0m HCl

(Radiometer C - Stem not waxed)

Final e.m.f. 0.6206
(0.1mV increase in 6 min.)

Solution	0.1m H_2SO_4	0.1mCl^-/E p_wH 9.41	0.1m H_2SO_4	1.0m HCl	0.1m H_2SO_4	0.1mCl^-/E p_wH 9.41
Time (min.)						
0	0.6200	0.6204	0.6199	0.6198	0.6200	0.6205
1	0.6205	0.6207	0.6205	0.6205	0.6206	0.6208
2	0.6206	0.6208	0.6206	0.6206	0.6207	0.6209
5	0.6206	0.6208	0.6206	0.6206	0.6207	0.6209
Final	0.6206 (8)	0.6208 (8)	0.6206 (11)	0.6207 (8)	0.6207 (7)	0.6208 (8)
ΔE(mV)	0.0	+0.2	-0.2	0.0	0.0	+0.2
Response	A + B	A + B	A + B	A + B	A + B	A + B

TABLE 6.2.

Electrode No. 17. 17/12/65. Initial Solution 0.1m H_2SO_4

(Radiometer B - Stem not waxed) Final e.m.f. 0.6246
(Constant 6 min.)

Solution	0.1m HBr	0.1mCl^-/T p_wH 8.76	0.1m H_2SO_4	11.0m HBr	0.1m H_2SO_4	0.1mCl^-/T p_wH 8.76
Time (min.)						
0	0.6243	0.6244	0.6247	0.6246	0.6244	0.6243
1	0.6245	0.6243	0.6246	0.6247	0.6246	0.6244
2	0.6246	0.6244	0.6246	0.6247	0.6246	0.6244
5	0.6246	0.6244	0.6246	0.6248	0.6247	0.6245
Final	0.6246 (8)	0.6244 (7)	0.6247 (7)	0.6248 (7)	0.6247 (8)	0.6245 (6)
ΔE(mV)	0.0	-0.2	+0.2	+0.1	-0.2	-0.2
Response	A + B	B	B	A + B	A + B	A + B

TABLE 6.3.

Electrode No. 30 17/8/66.

(Corning - Stem not waxed).

Initial Solution 0.5m HCl

Final e.m.f. 0.6724
(Constant 8 min.)

Solution	0.1m H_2SO_4	0.5mCl^-/E p_wH 9.93	0.1mCl^-/I 1.0m KCl p_wH 9.13
Time (min.)			
0	0.6765	0.6759	0.6764
1	0.6764	0.6763	0.6763
2	0.6764	0.6764	0.6763
5	0.6764	0.6765	0.6764
Final	0.6764 (8)	0.6765 (7)	0.6764 (7)
ΔE(mV)	0.0	+0.1	-0.1
Response	B	A + B	B

TABLE 6.4.

Electrode No. 21 12/11/65.

(Jena H - Stem not waxed).

Initial Solution 0.1mCl^-/E, p_wH 9.94.

Final e.m.f. 0.3591
(Constant 6 min.)

Solution	0.1m H_2SO_4	0.1mCl^-/E p_wH 9.94
Time (min.)		
0	0.3590	0.3591
1	0.3591	0.3592
2	0.3591	0.3592
5	0.3592	0.3592
Final	0.3592 (7)	0.3592 (8)
ΔE(mV)	0.0	0.0
Response	B	B

TABLE 6.5.

Electrode No. 29. 17/8/66.

(Jena HA - Stem not waxed)

Initial Solution 0.5m HCl

Final e.m.f. 0.4667
(Constant 8 min.)

Solution	0.1m H_2SO_4	0.5mCl^-/E p_wH 9.93	0.1mCl^-/T 1.0m KCl p_wH 9.13
Time (min.)			
0	0.4667	0.4665	0.4668
1	0.4667	0.4667	0.4667
2	0.4667	0.4668	0.4667
5	0.4667	0.4668	0.4667
Final	0.4667 (8)	0.4668 (8)	0.4667 (7)
ΔE(mV)	0.0	+0.1	-0.1
Response	B	A + B	B

TABLE 6.6.

Electrode No. 8. 14/4/66.

(E.I.L. GG 33 - Stem not waxed)

Initial Solution 0.1m H_2SO_4

Final e.m.f. 0.3558
(Constant 6 min.)

Solution	0.1mCl^-/T p_wH 8.68	0.1m H_2SO_4
Time (min.)		
0	0.3851	0.3850
1	0.3858	0.3857
2	0.3858	0.3858
5	0.3858	0.3858
Final	0.3858 (10)	0.3858 (9)
ΔE(mV)	0.0	0.0
Response	A + B	A + B

TABLE 6.7.

Electrode No. 8.

4/6/65

Initial Solution 0.1m HBr

(E.I.L. GG 33 - Stem waxed)

Final e.m.f. 0.3817
(0.1mV increase in 9 min.)

Solution	0.1m H_2SO_4	0.1m Br^-/E p_wH 9.72	0.1mCl^-/E p_wH 9.24	0.1mCl^-/E p_wH 9.75	0.1mCl^-/E p_wH 10.46	0.1m H_2SO_4
Time (min.)						
0	0.3817	0.3814	0.3815	0.3816	0.3817	0.3818
1	0.3817	0.3817	0.3818	0.3818	0.3820	0.3820
2	0.3818	0.3818	0.3819	0.3818	0.3820	0.3820
5	0.3818	0.3818	0.3819	0.3819	0.3820	0.3820
Final	0.3818 (7)	0.3818 (9)	0.3819 (9)	0.3819 (8)	0.3820 (7)	0.3820 (9)
ΔE(mV)	+0.1	0.0	+0.1	-0.1	+0.1	0.0
Response	B	A+B	A+B	A+B	A+B	A+B

TABLE 6.7. (Cont.)

Electrode No. 8.

(E.I.L. GG 33 - Stem waxed)

Solution	0.1m HBr	0.1m Br^-/E p_wH 9.72	0.1m H_2SO_4	0.1m Cl^-/E p_wH 9.75	0.1m H_2SO_4	0.1m Cl^-/E p_wH 10.46
Time (min.)						
0	0.3817	0.3819	0.3820	0.3820	0.3821	0.3823
1	0.3820	0.3820	0.3821	0.3821	0.3822	0.3824
2	0.3820	0.3821	0.3822	0.3822	0.3823	0.3824
5	0.3820	0.3821	0.3822	0.3822	0.3823	0.3824
Final	0.3821 (9)	0.3821 (8)	0.3822 (8)	0.3822 (8)	0.3823 (7)	0.3823 (8)
ΔE(mV)	0.0	0.0	0.0	0.0	+0.1	0.0
Response	A + B	A + B	B	A + B	A + B	B

the interval between first contact of a glass electrode with a new solution and making the first e.m.f. measurement was not more than 20 seconds. Hence the time scale actually used is merely displaced by a small constant interval relative to that with zero at the instant of transfer.

It can be seen that the response shown by the glass electrodes in tris and ethanolamine buffers was found to be no different from their response in acid standard solutions. Those electrodes which gave precise agreement with the hydrogen electrode when transferred between acid solutions also did so when transferred from acid to one of the alkaline buffer solutions. Furthermore the e.m.f. - time variations shown by a given electrode in the buffer solutions were similar to those for the same electrode in acid solutions. As was anticipated from the work of Caudle some electrodes gave e.m.f. - time variations which exhibited feature A followed by feature B and others gave e.m.f. - time variations which only contained feature B. In general it was found, in confirmation of the observations of Caudle, that the electrodes believed to have lithia glass membranes gave response of type A + B whereas the soda glass electrodes gave response B. However there were some exceptions to this. For example, the Jena HA electrode No.29, believed to have a lithia glass membrane usually gave response of type B (table 6.5). Also it was noticed that the E.I.L. GG 33 electrodes sometimes gave e.m.f. - time curves of type A + B although for most of these electrodes the transients were small (on average 0.3mV in 2 minutes) compared to those observed for the lithia glass electrodes.

With the exception of electrode No. 29 mentioned above, the Corning, Jena HA and Radiometer Band C electrodes all gave feature A which took the form of simple transients that did not change direction and lasted no more than about two minutes. Examples of the response of these electrodes in standard solutions are given in figure 8 and details of some of the transients are presented in table 6.8. This figure includes an example of a transient of type A produced by carrying out a transfer without actually changing the solution and a second example is to be found in figure 20. The magnitudes of these transients were somewhat dependent upon the individual electrode but the average size was about 1mV. The transients were followed by either a steady e.m.f. or, in a case where the asymmetry potential was changing, by an approximately linear drift of potential which could readily be extrapolated back to the instant of transfer to give an error of not greater than 0.2mV. For these electrodes, therefore, it was quite clear which part of the e.m.f. - time curve should be neglected when extrapolating the drift of e.m.f. back to the time of transfer.

However, as can be seen from figures 9 to 11 the other types of electrode believed to have lithia glasses gave feature A of a more complex nature usually including at least one turning point. This was particularly true for the Beckman E2 and Pye Ingold electrodes and in these cases it was difficult to decide which part of the e.m.f. - time curve should be neglected when applying the extrapolation procedure. The E.I.L. GHS 33 electrodes often gave transients of such long duration (about 10 minutes) that they

TABLE 6.8. Examples of Transients of Type A

Electrode No. 17. (Radiometer B).

E.m.f. Increase (mV.)	Time (min.)	E.m.f. Increase (mV.)	Time (min.)
0.4	3	0.7	2
0.4	2	0.3	2
0.9	3	0.3	2
0.8	2	0.6	2
1.8	2	0.4	2
1.0	3	0.4	2

Electrode No. 16. (Radiometer C).

E.m.f. Increase (mV.)	Time (min.)	E.m.f. Increase (mV.)	Time (min.)
0.6	2	0.5	3
0.5	2	0.4	3
0.7	2	0.2	1
0.8	2	1.0	2
0.7	2	0.3	2

TABLE 6.8. (Cont.) Examples of Transients of Type A.

Electrode No. 30. (Corning).

E.m.f. Increase (mV.)	Time (min.)	
0.4	3	This electrode also gave some results of type B.
0.3	3	
0.5	2	

Electrode No. 27. (Corning).

Stem Not Waxed		Stem Waxed	
E.m.f. Increase (mV.)	Time (min.)	E.m.f. Increase (mV.)	Time (min.)
0.8	3	2.2	2
0.4	2	1.4	2
0.4	1		
0.5	2		
0.4	2		
0.9	1		

obscured any real changes of asymmetry potential immediately after the transfers and made the extrapolation technique impossible. Furthermore it was found for some electrodes that the calibration e.m.f.

$$(Pt)\ H_2\ (p) \ \Big|\ \text{standard solution} \ \Big|\ \text{glass electrode}$$

was erratic with apparently sudden changes, as much as 0.5mV, resulting in the observation of non-reproducible errors in transfers between two solutions. This is illustrated by the results for the E.I.L. GHS 33 electrode No. 11 shown in figure 12. When transferred from 0.1m sulphuric acid to an ethanolamine buffer it gave an error of -0.5mV in the ethanolamine buffer but when it was transferred back to the sulphuric acid it gave an error of -0.2mV in the acid. Other examples of this type of behaviour are shown by the Beckman E2 electrode No. 19 (figure 9) and the E.I.L. GHS 33 electrode No. 18 (figure 11). This erratic behaviour combined with the transients of type A made it impossible to test the instantaneous potential idea with the Pye Ingold, Beckman E2 and E.I.L. GHS 33 electrodes.

Caudle carried out an extensive investigation of the so-called spurious transients, feature A, and recommended coating the electrode stem with paraffin wax as a method of reducing or eliminating them. In the present work, this procedure was found to be effective for certain electrodes which gave transients of a complex nature or which took an unusually long time to die away (5 minutes or more). Examples of the effectiveness of this procedure were found for both soda and lithia glass electrodes and waxing the electrode stem resulted in a substantial reduction of the transient

duration as well as a decrease in the magnitude of the potential change. For example, when its stem was not waxed, the Pye Ingold electrode No. 15 gave transients lasting about 5 minutes which changed direction, with an initial rapid fall in the glass electrode potential of an average 0.3mV, followed by a slow increase of about the same amount. These transients were reduced to a change of 0.2 or 0.3mV in one direction lasting only one minute, when the stem was waxed, as may be seen from comparison of figures 10 and 13. It was also found that one of the GG 33 electrodes (No. 14) gave type A + B response with transients larger than usual for that type of electrode but waxing its stem reduced these to about the same size as those observed with other GG 33 electrodes (figures 14 and 15).

The erratic behaviour observed with the Beckman E2 and E.I.L. GHS 33 electrodes was also reduced by waxing the electrode stems. This can be seen by comparing figures 16, 17 and 18 with those given earlier for the same electrodes. However, it will be observed that this procedure was not entirely successful. For example, electrode No. 11 gave instantaneous errors of 0.4mV when transferred between 0.5m HCl and 0.1m H_2SO_4 and 0.5mV when transferred between 1.0m HCl and 0.1m H_2SO_4 (figure 18). These were obtained by extrapolation of the e.m.f. - time curves neglecting the initial transients as indicated by the dotted lines in the figure. Similarly when the Beckman E2 electrode No. 19 was transferred from an ethanolamine buffer to 0.1m H_2SO_4, figure 16, the initial error neglecting the small transient was 0.3mV.

For other electrodes whose spurious transients were smaller and less

complex, waxing the stem apparently made no difference to the response observed for standard solutions. This is illustrated by the results for the Radiometer B electrode No. 17 shown in figures 19 and 20 and for the Corning electrode No. 27 given in table 6.8. It seems possible therefore that there are two effects, one of which is only apparent with certain electrodes and can be eliminated by waxing the stem, and the other which is smaller and observed with all electrodes even when their stems are waxed. Caudle suggested that these transients might be due at least in part to switching of the electrical circuit. However, it has been found that on switching the electrometer to measure the e.m.f. of a glass electrode cell some time after first placing the glass electrode in the solution, no transient is observed.

Although in most cases data for only one electrode of each type have been quoted, similar results were obtained with the other electrodes tested. On the basis of these results it was concluded that the Jena HA, Corning, Radiometer B and C and most soda glass electrodes are suitable for precise pH measurements in standard solutions. These electrodes agreed with the hydrogen electrode to within the precision of the experimental method and might show even greater accuracy if subjected to more rigorous testing.

The Beckman E2, E.I.L. GHS 33 and Pye Ingold electrodes only agreed with the hydrogen electrode to a precision dependent upon their individual limitations. For the Beckman E2 and E.I.L. GHS 33 electrodes the accuracy was about $\pm$0.5mV but for the Pye Ingold it was a little better than this. Some improvement

could be obtained by waxing the stems of these electrodes but, with the possible exception of the Pye Ingold, performance of these three types of electrode was still not as good as that of those electrodes listed earlier. Also since the better electrodes give satisfactory performance without the precaution of waxing their stems they will be preferred by those wishing to make precise measurements.

Once it had been established that tris and ethanolamine buffers could be used as standard solutions for testing glass electrodes, it then became of interest to investigate whether the electrodes were error-free up to an even higher pH in the absence of small inorganic cations. It was thought that solutions of the tetra-alkylammonium hydroxides, which are strong bases, would be suitable for this purpose. However these hydroxides are somewhat unstable and are not readily purified. Nevertheless a few experiments were carried out using a solution prepared from reagent grade tetraethylammonium hydroxide without any purification. An attempt was made to standardise the hydroxide by titration with 0.1m hydrochloric acid but although several different indicators were tried, it was found impossible to obtain a sharp end point since the colour change took place over the addition of about 1ml. of acid. This might have been due either to the presence of weaker bases formed by decomposition of the tetraethylammonium hydroxide, or to interaction between the organic base and the indicators. Nevertheless an approximately 0.1m solution of the hydroxide, which was also 0.1m in tetraethylammonium bromide, was prepared and it was found that a cell

containing this solution together with hydrogen and silver-silver bromide electrodes had a stable e.m.f. A few glass electrodes were therefore tested in this solution, and the results are given in tables 6.9 to 6.11.

It can be seen that the Jena HA and Radiometer B electrodes, both of which are thought to have lithia glass membranes, showed no error in the solution. However the soda glass electrode of type E.I.L. GG 33 (No. 8) gave a positive error of between 7 and 8mV. It is quite possible that this error was caused by a small quantity of inorganic cation present in the solution as an impurity. In fact the solution was subsequently analysed by flame photometry and was found to contain 20ppm of sodium, 1ppm of potassium and a trace of calcium. No other metals could be detected. A 1m sodium solution is equivalent to 20 parts in 10^3 and hence 20ppm corresponds to 0.001m. Since soda glass electrodes show errors of about 100mV and 50mV in 1m and 0.1m sodium solutions at pH 13, it is possible that the error observed with electrode No. 8 in the tetraethylammonium hydroxide was caused by the small concentration of sodium ions.

If a method of purifying the tetra-alkylammonium hydroxides could be found, it is possible that error-free results would be obtained for soda glass electrodes even at this high pH. Also it might be possible to standardise the hydroxide more accurately by a potentiometric titration, and certainly this method would show whether or not there is a sharp pH charge at the end point. If not, then this would suggest that the solution does in fact contain weaker bases formed by decomposition of the hydroxide.

TABLE 6.9.

Electrode No. 17. 21/1/66. Initial Solution 0.1m H_2SO_4

(Radiometer B - Stem not waxed)

Final e.m.f. 0.6249
(Constant 8 min.)

Solution	0.1m HBr	0.1m Cl^-/E p_wH 9.44	0.1m Br^- $(C_2H_5)_4NOH$ p_wH 13.14	0.1m Cl^-/E p_wH 9.44	0.1m HBr
Time (min.)					
0	0.6243	0.6247	0.6247	0.6244	0.6246
1	0.6249	0.6249	0.6249	0.6248	0.6250
2	0.6250	0.6250	0.6250	0.6250	0.6250
5	0.6250	0.6250	0.6250	0.6250	0.6251
10	0.6250	0.6251	0.6250		
Final	0.6250 (10)	0.6251 (15)	0.6250 (11)	0.6251 (9)	0.6251 (8)
ΔE(mV)	+0.1	0.0	-0.1	0.0	0.0
Response	A+B	A+B	A+B	A+B	A+B

TABLE 6.10.

Electrode No. 22.

21/1/66.

Initial Solution 0.1m H_2SO_4

Final e.m.f. 0.4846
(Constant 8 min.)

(Jena HA - Stem not waxed)

Solution	0.1m HBr	0.1m Cl^-/E p_wH 9.44	0.1m Br^- $(C_2H_5)_4NOH$ p_wH 13.14	0.1m Cl^-/E p_wH 9.44	0.1m H_2SO_4	0.1m Br^- $(C_2H_5)_4NOH$ p_wH 13.14	0.1m Cl^-/E p_wH 9.44
Time (min.)							
0	0.4825	0.4850	0.4855	0.4800	0.4822	0.4863	0.4800
1	0.4844	0.4851	0.4850	0.4838	0.4845	0.4851	0.4842
2	0.4845	0.4848	0.4849	0.4842	0.4846	0.4849	0.4845
5	0.4846	0.4846	0.4847	0.4845	0.4847	0.4848	0.4847
10		0.4845	0.4848	0.4845		0.4848	0.4847
Final	0.4846 (9)	0.4845 (12)	0.4848 (12)	0.4845 (15)	0.4847 (8)	0.4848 (10)	0.4847 (10)
ΔE(mV)	0.0	-0.1	+0.2	-0.3	+0.2	+0.1	-0.1
Response	A + B	A + B	A + B	A + B	A + B	A + B	A + B

TABLE 6.11.

Electrode No. 8.

21/1/66

Initial Solution 0.1m H_2SO_4

(E.I.L. GG 33 - Stem not waxed)

Final e.m.f. 0.3844
(Constant 10 min.)

Solution	0.1m HBr	0.1m Cl^-/E p_wH 9.44	0.1m Br^- $(C_2H_5)_4NOH$ p_wH 13.14	0.1m Cl^-/E p_wH 9.44
Time (min.)				
0	0.3847	0.3843	0.3917	0.3851
1	0.3843	0.3843	0.3915	0.3850
2	0.3843	0.3844	0.3917	0.3850
5	0.3844	0.3845	0.3921	0.3850
10		0.3845	0.3924	
Final	0.3844 (8)	0.3845 (10)	0.3927 (15)	0.3850 (9)
ΔE(mV)	0.0	+0.1	+6.8*	-7.6
Response	A + B	B	C_1	E

Summary of Test in Tetraethylammonium hydroxide

E.m.f. variation:-
0.2mV decrease (1 min.)
1.2mV increase (14 min.)

Final error:-
+7.9 ± 0.3 mV.

*By extrapolation neglecting the slight initial decrease in e.m.f.

Although this investigation has been mainly concerned with the response of glass electrodes in the alkaline pH range, some experiments have been carried out with a limited number of concentrated acid solutions. Since Caudle did not test specimens of certain types of electrode employed in the present work, some of these results will be briefly mentioned. The soda glass electrodes used here were of types already examined by Caudle and as was expected from this work they showed errors in concentrated acid solutions, and these will be discussed later. However it is appropriate here to point out that during the early part of this work 0.1m HCl was thought to be suitable as a standard solution for soda glass electrodes, since Caudle had reported that the error shown by these electrodes in HCl solutions do not appear until a concentration of about 1 molal. However, although the soda glass electrodes were initially error-free in 0.1m HCl they began to show errors in this solution as they became older, and for this reason 0.1m HCl was abandoned in favour of sulphuric acid (1.0 or 0.1m) or 0.1m HBr as an acid standard solution for these electrodes. In fact these solutions were also employed as acid standard solutions when testing the lithia glass electrodes, 0.1m H_2SO_4 being the one used most frequently.

The most striking result for a lithia glass electrode in concentrated acid solution was that obtained for the Radiometer B electrode No. 17 in 11m HBr. The data for this test are included in table 6.2 and it is seen that within the accuracy of the experimental method the electrode was error-free in this solution. Some of the other lithia glass electrodes were tested

in HCl solutions of concentrations up to 1 molal and again no errors were observed.

A few experiments have also been carried out using buffered magnesium sulphate solutions, as in 1937 Amis and Gabbard had reported that electrodes made from Corning 015 glass showed errors in concentrated solutions of this salt. In the present work, several electrodes of different types were tested in 1.7 - 1.9m $MgSO_4$ solutions buffered with either tris or acetic acid and sodium acetate, and as is shown in tables 6.12 to 6.17 they all gave error-free results.

In this section it has been shown that tris and ethanolamine buffers may be used as standard solutions for glass electrodes. The response of various types of commercial glass electrode, when transferred between standard solutions of widely different pH, has been compared and those best suited to precise measurements have been selected. The question of whether the response of an electrode in a solution where it shows an error, is influenced by the pH of the standard solution from which it has been transferred, will be considered in the next section.

TABLE 6,12.

Electrode No. 1. 21/1/64.

(E.I.L. GG 33 - Stem not waxed)

Initial Solution 0.1m HCl

Final e.m.f. 0.4056
(Constant 8 min.)

Solution	1.7m $MgSO_4$ p_wH 9.02	0.1m HCl	1.7m $MgSO_4$ p_wH 9.02
Time (min.)			
0	0.4061	0.4040	0.4070
1	0.4058	0.4050	0.4055
2	0.4057	0.4053	0.4054
5	0.4056	0.4053	0.4053
Final	0.4056 (8)	0.4053 (6)	0.4053 (6)
△E(mV)	+0.1	-0.3	0.0
Response	A + B	A + B	A + B

TABLE 6,13.

Electrode No. 8. 3/8/66.

(E.I.L. GG 33 - Stem not waxed)

Initial Solution 0.1m H_2SO_4

Final e.m.f. 0.3881
(Constant 8 min.)

Solution	Acetate 1.0m Na^+ p_wH 4.75	1.87m $MgSO_4$ p_wH 4.16
Time (min.)		
0	0.3877	0.3878
1	0.3880	0.3878
2	0.3880	0.3878
5	0.3880	0.3878
Final	0.3880 (7)	0.3878 (7)
E(mV)	-0.1	-0.2
Response	A + B	B

TABLE 6.14

Electrode No. 16. 3/8/66.

(Radiometer C - Stem not waxed)

Initial Solution Acetate, 1.0m Na^+, p_wH 4.75

Final e.m.f. 0.6076
(0.2mV increase in 9 min.)

Solution	1.87m $MgSO_4$ p_wH 4.16	0.1m H_2SO_4
Time (min.)		
0	0.6073	0.6076
1	0.6074	0.6077
2	0.6075	0.6077
5	0.6076	0.6078
Final	0.6076 (8)	0.6078 (8)
ΔE(mV)	-0.2	+0.1
Response	A + B	B

TABLE 6.15.

Electrode No. 16. 12/9/66.

(Radiometer C - Stem not waxed)

Initial Solution 0.5mCl^-/T, p_wH 8.15.

Final e.m.f. 0.6281
(0.2mV decrease in 5 min.)

Solution	1.85m $MgSO_4$ p_wH 8.43	0.1m H_2SO_4	0.1mCl^-/T p_wH 8.15
Time (min.)			
0	0.6076	0.6079	0.6076
1	0.6078	0.6080	0.6079
2	0.6079	0.6081	0.6081
5	0.6079	0.6082	0.6081
	0.6080 (50)	0.6082 (10)	
Final	0.6080 (56)	0.6082 (11)	0.6081 (8)
ΔE(mV)	-0.1	+0.1	-0.1
Response	A + B	B	A + B

TABLE 6.16.

Electrode No. 17. 14/9/66

(Radiometer B - Stem not waxed)

Initial Solution 0.1m H_2SO_4

Final e.m.f. 0.6275
(Constant 7 min.)

Solution	0.5m Cl^-/T p_wH 8.15	1.85m $MgSO_4$ p_wH 8.43
Time (min.)		
0	0.6267	0.6268
1	0.6273	0.6272
2	0.6275	0.6273
5	0.6275	0.6274
	0.6275 (12)	
Final	0.6275 (15)	0.6274 (7)
ΔE(mV)	0.0	-0.1
Response	A + B	A + B

TABLE 6.17.

Electrode No. 27. 12/9/66.

(Corning - Stem not waxed)

Initial Solution 0.1m H_2SO_4

Final e.m.f. 0.6759
(Decreased 0.2mV in 5 min.)

Solution	0.5m Cl^-/T p_wH 8.15	1.85m $MgSO_4$ p_wH 8.43
Time (min.)		
0	0.6755	0.6750
1	0.6758	0.6759
2	0.6759	0.6759
5	0.6759	0.6758
Final	0.6759 (6)	0.6757 (7)
E(mV)	0.0	0.0
Response	A + B	A + B

6.2. The response in Acid and Alkaline Solutions (Errors).

The work of Caudle and Zielen has demonstrated that the deviations shown by pH responsive glass electrodes in acid solutions cannot be explained simply as changes of asymmetry potential as was suggested by Beck and Wynne-Jones. It therefore seemed unlikely that the alkaline errors could be explained in this way and the first object of the present work was to confirm this. Once it had been established that the deviations shown by glass electrodes in alkaline solutions were in fact real errors and not changes of asymmetry potential, it was proposed to carry out a general survey of the errors shown by different types of electrode in a variety of alkaline solutions. In several instances the experiments carried out by previous workers were repeated when it was thought that the earlier data were unreliable.

It has been stated by many previous workers that the magnitude of the error, shown by a glass electrode in an alkaline solution, depends upon the nature of the cation in the solution and increases with increasing cation concentration and pH. These observations have been confirmed in the present investigation. The dependence of the error upon the pH and the nature of the cation in the solution can be clearly seen from the results as a whole, presented graphically and in tabulated form in this and subsequent chapters, and data which demonstrate that for a given cation, the error increases with cation concentration, are given in tables 6.18 and 6.19.

However, as was pointed out in chapter 2, although it has long been

- Dependence of Alkaline Errors on Cation Concentration

TABLE 6.18

0.1m and 1.0m Sodium Solutions at pH 10

Electrode No. 5. (E.I.L. GG 33)

0.1m Na^+				1.0m Na^+			
Date	Test	p_wH	Error (mV)	Date	Test	p_wH	Error (mV)
				21/12/65	185	9.84	+6.3
6/5/66	217	10.31	+4.2				
				6/5/66	216	10.55	+17.8

Electrode No. 8. (E.I.L. GG 33)

0.1m Na^+				1.0m Na^+			
Date	Test	p_wH	Error (mV)	Date	Test	p_wH	Error (mV)
				10/8/65	139	9.85	+5.4
5/5/66	214	10.31	+3.5				
				5/5/66	213	10.55	+16.6

TABLE 6.18 Cont.

Electrode No. 9. (Jena H)

0.1m Na^+				1.0m Na^+			
Date	Test	p_wH	Error (mV)	Date	Test	p_wH	Error (mV)
				22/12/65	190	9.84	+4.5
22/4/66	209	10.31	+2.3				
				22/4/66	208	10.55	+11.2

Electrode No. 16. (Radiometer C)

0.1m Na^+				1.0m Na^+			
Date	Test	p_wH	Error (mV)	Date	Test	p_wH	Error (mV)
				10/8/65	59	9.85	+3.0
5/5/66	57	10.31	+2.0				
				5/5/66	56	10.55	+7.1

TABLE 6.19.

Dependence of Alkaline Errors on Cation Concentration

1.0m and 2.0m Potassium Solutions at pH 10.6

E.I.L. GG 33 Electrodes

Electrode	1.0m K^+				2.0m K^+			
	Date	Test	p_wH	Error (mV)	Date	Test	p_wH	Error (mV)
No.1	13/7/65	117	10.54	+4.5	13/7/65	118	10.65	+6.7
No.5	18/6/65	108	10.56	+7.0	18/6/65	109	10.65	+9.9
					13/7/65	120	10.65	+10.0
No.8	14/6/65	104	10.56	+3.8	18/6/65	111	10.65	+5.2
	18/6/65	110	10.56	+4.1				

accepted that the alkaline error shown by a glass electrode was dependent upon the nature of the cation in solution, there has been some doubt concerning the relative magnitudes of the errors of lithia glass electrodes for solutions of sodium and lithium ions. This has accordingly been re-examined. On the other hand, it was thought unnecessary to obtain further data to demonstrate the dependence of the error upon the cation concentration. It was therefore decided to test the glass electrodes in series of solutions of increasing pH containing the same concentration of different alkali metal cations. Since in most previous investigations the time dependence of the glass electrode errors has not been considered, this feature has received particular attention here.

It was also found in this work that the error observed for a given alkaline solution varied between the different types of electrode tested. This was to be expected since it is well established that the magnitudes of the errors are dependent upon the composition of the glass membrane. However, it was not possible to investigate the dependence of the errors upon glass composition using commercial electrodes, since the manufacturers were unwilling to disclose details of their electrode glasses.

In view of the factors discussed in the foregoing paragraphs, the present investigation has been primarily concerned with the following features of glass electrode response.

1. The time dependence of the errors;

2. their reproducibility both between different electrodes of the same

type, and for repeated testing of an individual electrode in the same solution;

3. comparison of the response of different manufacturers' electrodes and;

4. comparison of the magnitudes of the errors shown by electrodes in solutions containing different cations.

A constant cation concentration of 1 molal was selected and electrodes were tested in sodium, potassium and lithium solutions of this concentration. Experiments with potassium solutions were, however, limited to soda glass electrodes, and these electrodes were also tested in certain acid solutions in which they showed errors. Each experimental run usually included two standard solutions and the pH response of the glass electrodes was checked in these solutions before testing in the acid or alkaline solutions commenced. In general, testing of electrodes was confined to those solutions where the errors were not too large (i.e. 20-30mV) since it was thought possible that larger errors would be accompanied by substantial permanent changes in the glass surface which might partially invalidate comparison of results obtained on different occasions with the same electrode. Furthermore large errors are not usually encountered during normal pH measurements.

In lithium solutions all the electrodes tested began to show errors at about the same pH (10-11), but in sodium solutions the pH's at which the different electrodes first showed errors, were spread over a wider range as shown in figure 21. Hence the pH at which the errors first appeared in the

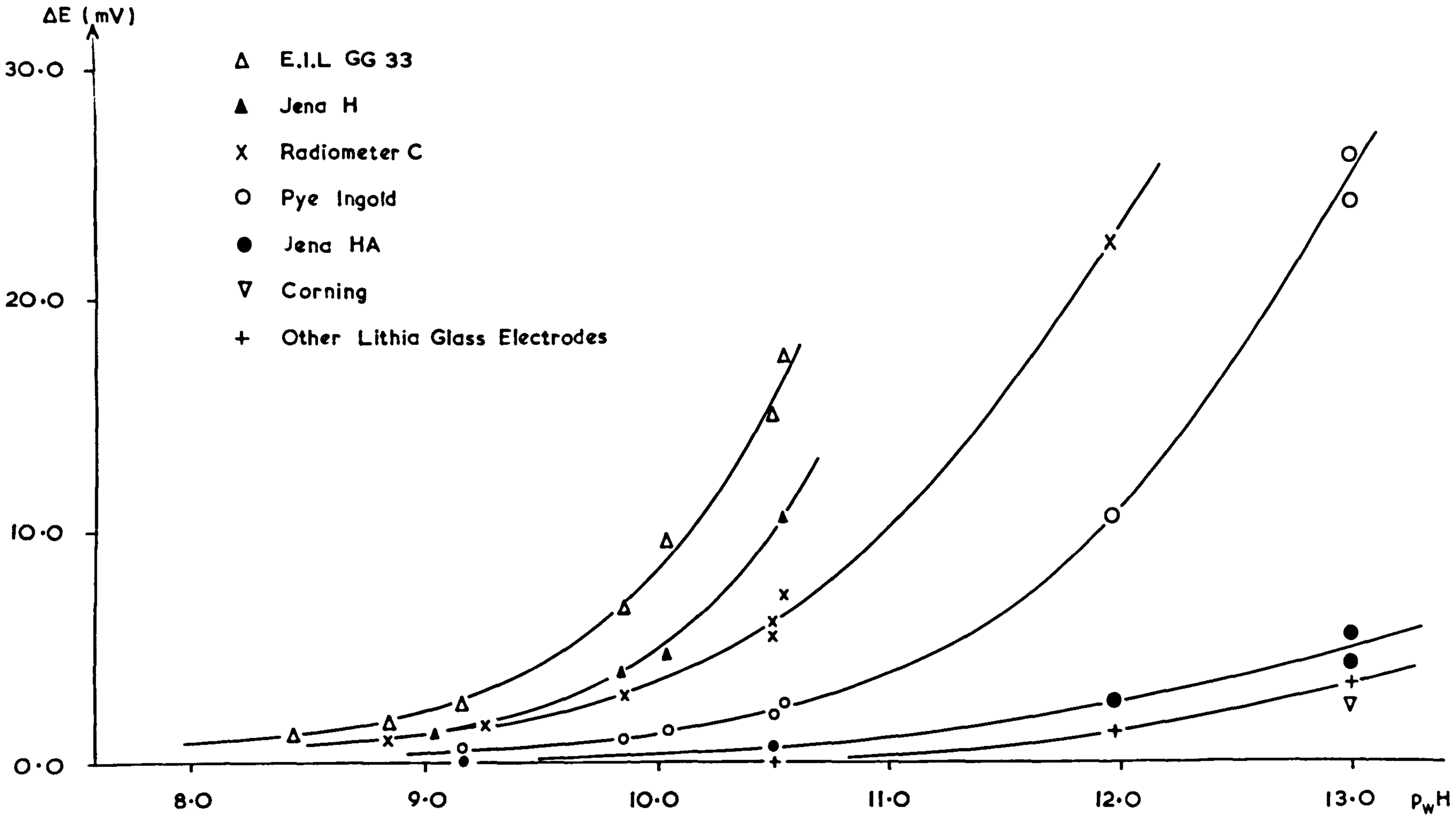


Fig. 21 The Errors of Glass Electrodes in 1·0m Na^+ Solutions.

1m sodium solutions, or alternatively the relative magnitudes of the sodium and lithium errors, could be used to characterise the different types of commercial electrode tested. In this way it was found that the glass electrodes could be divided into three groups.

Group 1: These electrodes showed no errors in sodium and lithium solutions below pH 11 and above this pH gave much larger errors in lithium solutions than in sodium solutions of the same pH. The following electrodes, which are all believed to have lithia glass membranes, form this group.

Beckman E2.
Corning.
E.I.L. GHS 33.
Jena HA.
Radiometer B.

Group 2: The electrodes of this group gave errors in sodium and lithium solutions below pH 11 and for a given electrode or type of electrode the sodium and lithium errors were of about the same magnitude at any particular pH. The Radiometer C and Pye Ingold electrodes fall into this category and these are also thought to be made from lithia glasses.

Group 3: These electrodes showed much larger errors in sodium solutions than in lithium solutions of the same pH. The errors in sodium solutions first appeared around pH 8 and were larger than the sodium errors of any of the other electrodes tested. Both the E.I.L. GG 33 and Jena H electrodes which form this group have soda glass membranes.

Most of the errors were not constant but showed a time variation which was usually most rapid immediately after an electrode had been placed in a

new solution. In most instances when a time variation was observed the error finally reached an approximately constant value and comparison of the magnitudes of the errors shown by the various electrodes has in general been based upon these final values. However, the e.m.f. variations, although sometimes quite marked, were not large compared to the differences in the magnitudes of the errors shown by the three main groups of electrode listed above, and hence they do not make the classification ambiguous. The transients associated with the errors of glass electrodes in both acid and alkaline solutions were in general so large as to obscure any spurious effects designated as feature A. Hence waxing the stem of an electrode was found to have no influence upon its response in these solutions.

A number of experiments were carried out in order to determine whether the nature of the standard solution had any influence upon the response of an electrode in an alkaline solution where it showed an error. For this purpose a single glass electrode was tested more than once in the same solution using two standard solutions, one having a pH similar to that of the test solution and one having a completely different pH. For some such tests, the standard solution was an acid, usually 0.1m H_2SO_4, whereas in others it was an alkaline solution buffered with tris or ethanolamine. It was found that the magnitude of the error shown by a glass electrode in a test solution was independent of the nature of the standard solution employed. Also there was no apparent correlation between the standard solution and the time dependence of the e.m.f. either for the test solution or after

transferring the glass electrode back to the standard solution. The data obtained for duplicate tests of this kind are to be found in the tables presented in the results chapters which follow and will be referred to again there, when appropriate.

In addition to investigating the effect of varying the standard solution, some experiments have been carried out to show that the response of an electrode in an alkaline solution, is independent of both the buffer used to fix the pH, and the anion present in the solution. For the first of these, some electrodes were tested in tris and borax buffers having the same pH and cation content, and for the second electrodes were tested in two 1 molal potassium solutions both buffered to the same pH with ethanolamine, but having different anions, namely chloride and bromide. All these experiments involved soda glass electrodes and the results are given in detail in chapter 8.

Finally, since the use of ion-exchange resins for the purification of water, tends to introduce small amounts of organic impurities, some experiments were carried out using solutions prepared from triple distilled water. These experiments involved two groups of solutions which were identical except for the method used to purify the water. One of these groups of solutions was prepared using deionised water in the usual way, and the other group was prepared with triple distilled water. The latter solutions were used in the experimental runs on the 11th. and 19th. May 1965 and the response of the glass electrodes in these solutions appeared to be no different to

their response in the corresponding solutions prepared with deionised water (17/5/65 and 21/5/65).

In the following three chapters, the errors observed for pH responsive glass electrodes will be considered in more detail. The e.m.f.-time variations will be described, as far as possible, in terms of the principle features outlined in section 5.4. Although it is desirable to have a system such as this for classifying the main features of the e.m.f.-time variations observed with glass electrodes, such a classification cannot take account of all the details of the data, since a very wide range of e.m.f.-time variations have been observed. For this reason, the data obtained for tests of the pH responsive glass electrodes in solutions in which they showed errors, have been presented in tabulated form as an appendix. There is no doubt that this method of presenting the data does not reveal all the details of the e.m.f.-time variations, which can only be seen from the actual pen recorder traces. However it clearly would not be practicable to present all the data graphically and the pen recorder traces are available for inspection by those who may require further details of these results.

The principal features of the data obtained for the different types of pH responsive glass electrode are presented in the three results chapters which follow. The transients will be characterised by tabulating the e.m.f. variations and their duration. As was stated in chapter 4, e.m.f. readings were made to the nearest 0.1mV. However the initial errors were often not as accurate as this on account of the rapid variations of e.m.f. frequently

observed immediately after glass electrode transfers. In general the accuracy of the initial errors is about ±0.3mV. The uncertainty in the initial variation of e.m.f. after a glass electrode has been transferred to a new solution is determined by the uncertainty in the initial error and is therefore about ±0.3mV also. The duration of the transients may be regarded as being accurate to about ±1 min. and in general, the smaller the time the smaller the uncertainty. The final approximately constant errors shown by the electrodes in the various solutions, have also been tabulated. These were calculated using the procedure described in section 5.4. (page 103) and the values may be regarded as having an accuracy of about ±0.3mV (i.e. ±0.005 of a pH unit).

Those who require further details of the results are referred to the appendix where the data are given in the form of errors at various times after transfer relative to the final e.m.f. observed for the glass electrode in the previous standard solution. That is, when an electrode was tested in a solution where it showed an error, both the e.m.f. values at various times for the test solution and those for the standard solution 2 of that experiment are given as the errors relative to the final e.m.f. observed with the glass electrode in standard solution 1. This method has been preferred to the procedure of always giving the error relative to the final e.m.f. in the previous solution, because the response observed when an electrode is transferred from a test solution to a standard solution, has been regarded as complementary to that shown for the test solution itself.

Hence the method used gives a clearer picture of the data. It may be pointed out that the final value recorded for standard solution 2 gives the overall change in asymmetry potential and calibration e.m.f. for the duration of the experiment. Each test of a pH responsive glass electrode has been numbered to facilitate reference both between the various tables in the results chapters and between these tables and the appendix.

The first of the more detailed results chapters that follow will be concerned with the lithia glass electrodes, since by virtue of their smaller errors in both acid and alkaline solutions, these have now largely superseded soda glass electrodes for pH measurement. Several of these types of electrode commercially available, are supplied together with nomographs which specify the magnitudes of the errors shown in alkaline sodium solutions. It is intended that this data should be regarded as a series of empirical factors which may be used to correct an observed pH reading to the value that would be obtained using a hydrogen electrode. Since glass electrode errors often show a marked time dependence, it is clearly necessary to know the time to which these correction factors refer, and this is usually not clearly stated. Also the precision with which pH measurements may be made using this procedure depends upon the reliability of the correction factors and hence the reproducibility of the glass electrode errors. The quantitative data are limited to sodium solutions and only qualitative information is given concerning the relative magnitudes of the errors in solutions containing different cations.

The choice of experiments for the lithia glass electrodes was partly determined by the above considerations. The relative magnitudes of the errors shown by the various types of electrode, or conversely the pH ranges over which the various electrodes are error-free in solutions of different cations, was first of all investigated. Secondly it was thought particularly important with these electrodes to examine the time dependence and reproducibility of the errors.

The study of the response of soda glass electrodes is now mainly of academic interest in that the data obtained might shed some light upon the functioning of glass electrodes in general. Nevertheless, the features mentioned above for lithia glass electrodes were still of some interest, and it was also possible to investigate whether there was any correlation between the acid and alkaline errors shown by the same electrodes. During experimental runs when soda glass electrodes were tested in both acid and alkaline solutions, it was observed that the response of an electrode in alkaline solutions was influenced by its previous treatment in acids. It has been shown that if a soda glass electrode is placed in an acid solution in which it shows an error, e.g. 1m HCl or 5m HBr, that both the magnitude and the time variation of the errors shown in alkaline solutions are increased as a result. The change is only temporary and the electrode recovers its former response characteristics in alkaline solutions after about one week. Hence, this factor had to be borne in mind when testing soda glass electrodes in alkaline solutions, and in order to obtain data

that represented general or typical response, it was important that an electrode should not have been placed in an acid solution where it showed an error, for at least one week previous to testing in alkaline solutions. The alkaline errors of soda glass electrodes under normal conditions will be described in chapter 8, and chapter 9 will be concerned with the acid errors, and their influence upon the response of the electrodes in alkaline solutions.

CHAPTER 7

Alkaline Errors shown by Lithia Glass Electrodes

In the last chapter it was explained that the different types of pH responsive glass electrodes tested in this work could be divided into three groups according to the magnitudes of their errors in alkaline solutions containing sodium or lithium ions. Those electrodes which are believed to have lithia glass membranes formed the first two of these groups. The suitability of these electrodes for making precise measurements in the intermediate pH range has already been discussed and their response in alkaline solutions where they show errors will now be considered.

Usually two electrodes of each type were tested both when investigating the precision of their pH response in standard solutions and for experiments with alkaline solutions containing sodium ions. This was thought advisable since a single electrode would not necessarily be typical of all the electrodes in a batch. However if two electrodes of a particular type were compared in both standard solutions and alkaline sodium solutions and found to exhibit similar response characteristics, then usually only one of the two electrodes was tested in lithium solutions. Furthermore, for electrodes from group 1, experiments with lithium solutions were limited to examples of the Corning, Jena HA and Radiometer B electrodes which had been found to be the most suitable for precise pH measurements in standard solutions.

The variations of potential shown by these lithia glass electrodes during experiments with alkaline solutions in which they gave errors, were found to

be limited to a few different types. However, as will be seen, none of these types of response were specific to either of the two groups into which these electrodes have been divided according to the magnitudes of their errors. In fact, all the lithia glass electrodes except the Corning from group 1 and the Radiometer C from group 2, gave the type D_1 response (or D_1 + E) shown in figure 22. Hence this type of response was shown by some electrodes from each group but in neither group was the same type of response shown by all the electrodes.

The data obtained when testing the various lithia glass electrodes in alkaline solutions will be presented in the first three sections of the chapter with the electrodes arranged according to the types of response. The results for the electrodes which gave the type D_1 response outlined above, will be considered first since this type of response was the most common. Finally in section 7.4. the relative magnitudes of the errors shown by the various electrodes, will be discussed and it will be explained how this has been used as a basis for dividing the electrodes into the two groups mentioned above.

7.1. Electrodes which showed Type D_1 Response.

Except in a few experiments where the e.m.f.-time variations were sufficiently small to be described as type E, these electrodes almost invariably gave type D_1 transients both on transfer to a test solution and after transfer back to a standard solution, and this behaviour was associated with the errors

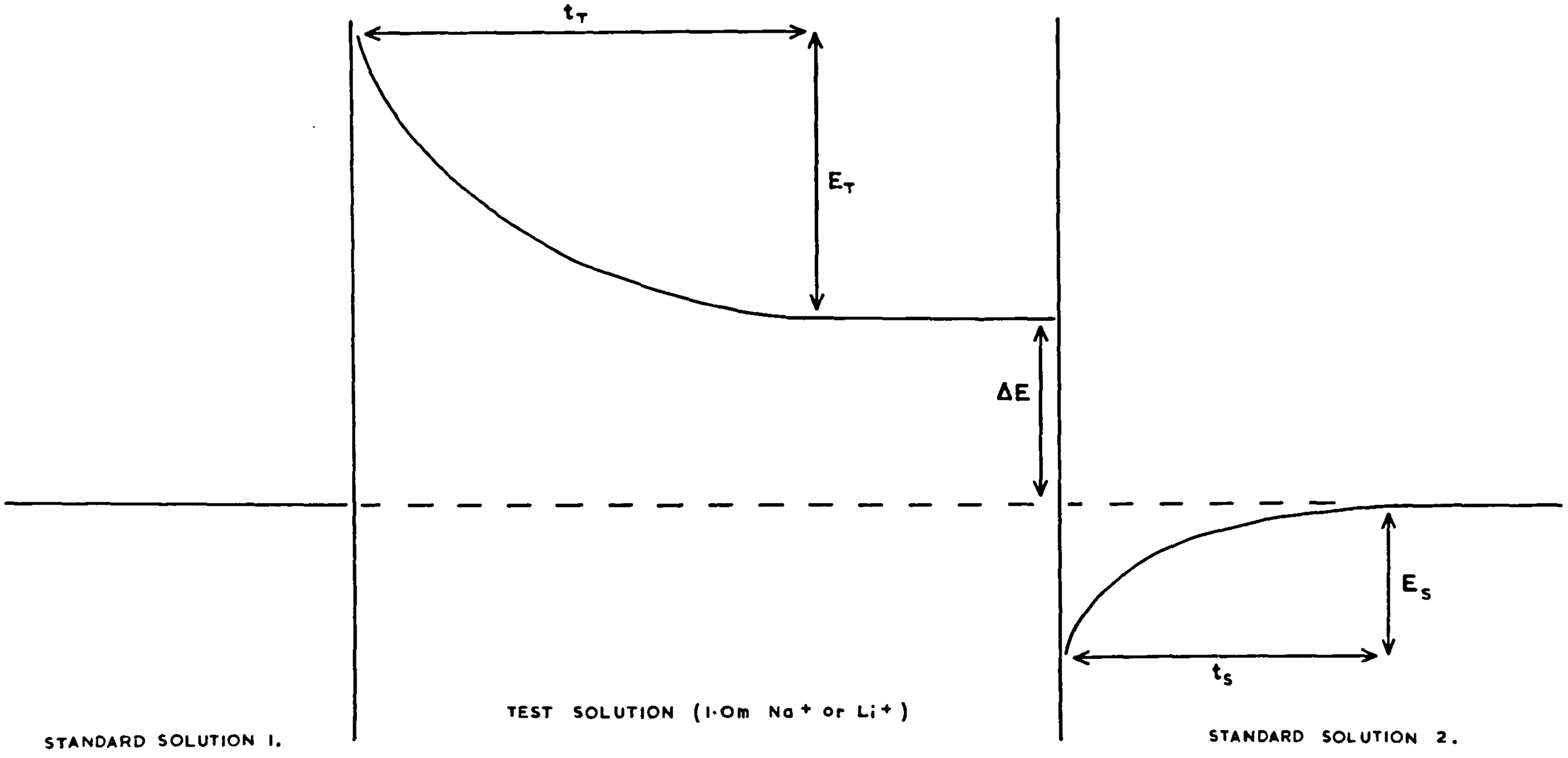


Fig. 22 The Response of Most Lithia Glass Electrodes in Alkaline Solutions.

in both sodium and lithium solutions. Only when the errors were less than about 1mV, were other types of response observed, but in these experiments the electrochemical effects would be small and hence electrical effects (feature A) may have made a significant contribution to the e.m.f.-time curves. Hence, apart from these few exceptions, the error shown by one of these electrodes in an alkaline test solution, decreased at a decreasing rate and the e.m.f.-time curve tended towards a point at which $\left|\frac{dE}{dt}\right|$ became zero. This was regarded as the end of the transient, since any subsequent e.m.f. variation was small. In some experiments this point was actually observed, but in others the error was still decreasing when the electrode was transferred back to a standard solution. The end of the transient for the standard solution was regarded as the point at which the e.m.f. either became constant or the time-variation became slight and approximately linear.

The transients shown by these electrodes have been characterised in tables 7.1 and 7.2, by recording in each case the change in e.m.f. and the time taken for the transient to die away. These quantities have been termed E_T and t_T for the transient observed with the test solution and E_S and t_S for that subsequently obtained with the standard solution, as indicated in figure 22. If the value of t_T is underlined then the end of the transient for the test solution was not observed, and the figure stated is then the total time for which the glass electrode was placed in that solution. As was explained in section 6.2., these quantities cannot be specified very accurately but nevertheless give a general indication of the magnitudes of

TABLE 7.1.

Type O_1 Transients shown by Lithia Glass Electrodes

Experiments with 1.0m Sodium Solutions

ΔE, E_T and E_S in mV, t_T and t_S in minutes

Beckman E2.

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 3	11.97	25/11/65	72	+1.5	1.3	10	1.0	4
	13.00	25/11/65	73	+3.1	3.1	40	2.8	10
Electrode No. 19	11.97	22/11/65	20	+1.4	0.6[x]	5	0.8	10
		22/11/65	21	+1.6	1.9	5	0.4	8
	13.00	12/11/65	74	+2.6	3.1	18	1.9	9

E.I.L. GHS 33

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 18	11.97	25/11/65	22	+1.0	1.1[x]	13	2.0[x]	10
	13.00	25/11/65	23	+2.9	2.2[x]	45	3.5[x]	12

[x] 0.1m Cl^-/Ethanolamine + 1.0m NaCl p_wH 10.52 used as standard solution

TABLE 7.1. (Cont.)

Jena HA

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 22	11.97	25/11/65	18	+2.6	2.1	18	2.3	8
	13.00	25/11/65	19	+5.4	6.7	50	4.1	15
		12/9/66	24	+4.2	5.4	35	2.8	15
		12/9/66	25	+3.7	5.9*	30	4.8*	14
Electrode No. 29	13.00	15/9/66	46	+3.0	7.9	55	1.8	12

Radiometer B

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 4	11.97	22/11/65	12	+1.6	2.0	8	1.5	5
	13.00	22/11/65	13	+3.4	2.7	21	2.8	8
Electrode No. 17	11.97	18/11/65	6	+1.5	0.4×	3	0.6×	4
		18/11/65	8	+1.3	0.4×	6	-	
	13.00	1/11/65	2	+4.6	4.2	32	1.9	12
		18/11/65	7	+4.0	3.2×	23	2.4×	9
		14/9/66	26	+4.9	4.6	36	0.8	10
		14/9/66	27	+4.5	5.2*	80	1.7*	15

× 0.1m Cl^-/Ethanolamine + 1.0m NaCl p_wH 10.52 used as standard solution

TABLE 7.1. (Cont.)

Pye Ingold

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 10	9.85	30/7/65	64	+0.8	1.5*	10	1.0*	10
	10.49	4/8/65	65	+2.1	2.0	10	1.2	2
		5/8/65	68	+2.0	1.4	13	1.7	8
	13.00	14/9/66	29	+26.1 ±0.5	9.3	124	6.2	18
Electrode No. 15	9.85	4/8/65	66	+1.0	0.5	2	0.7	7
	10.04	1/11/65	5	+1.3	E		1.2	7
	10.49	4/8/65	67	+1.9	1.0	3	1.1	11
	10.52	22/11/65	14	+2.0	1.6	10	1.3	6
	10.55	5/5/66	39	+2.5	1.5	2	1.0*	8
	11.97	22/11/65	15	+10.7	3.8	19	3.3	16
		22/11/65	16	+10.4	4.6	25	3.3	20
	13.00	1/11/65	4	+24.0	9.7	3½ hrs.	6.9	30

TABLE 7.2.

Type D_1 Transients shown by Lithia Glass Electrodes

Experiments with 1.0m Lithium Solutions

ΔE, E_T and E_S in mV. t_T and t_S in minutes.

Jena HA

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 22	10.20	11/5/66	34	+0.1	1.5	6	0.4	2
	11.81	11/5/66	32	+6.2	2.6	10	4.6	7
	12.81	11/5/66	33	+20.4	7.1	21	4.4	13

Radiometer B

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 17	11.81	27/5/66	35	+5.2	E		1.1*	8
		27/5/66	36	+5.4	0.8	4	1.8	10
	12.81	5/5/66	31	+16.6	1.7×	5	1.4	5
		14/9/66	28	+14.4	6.1*	20	7.4*	15

Test 28 for Electrode No. 17 was a special case and is discussed in detail in the text.

× 0.1m Cl^-/Ethanolamine + 0.1m NaCl p_wH 10.31 as standard solution.

TABLE 7.2. (Cont.)

Pve Ingold

	p_wH	Date	Test	ΔE	E_T	t_T	E_S	t_S
Electrode No. 10	12.81	14/9/66	30	+24.4	5.4	65	6.0	13
Electrode No. 15	10.59	19/8/65	261	+0.9	0.5	1	0.4	6
		24/8/65	262	+0.9	0.8	2	0.7	5
	11.81	27/5/66	37	+8.0	1.3	19	3.0*	10
	12.81	5/5/66	38	+26.5	5.0	40	7 ± 1	15

the transients.Where the details of a transient are marked with an asterisk, the electrode was transferred either from or to sulphuric acid as standard solution, whereas in other cases an alkaline standard solution was employed, unless otherwise stated. This procedure has been used in all other tables of transients in this chapter. The tables 7.1 and 7.2 also include values of the final error (ΔE) for each experiment calculated in the manner described in section 5.4. The precision of these values will be considered later.

An example of a result in which part of the e.m.f.-time variation observed for the test solution might be regarded as a change of asymmetry

potential, was test No. 28 for electrode No. 17 in 1.0m lithium solution at p_wH 12.81. The electrode was left in the solution for 127 minutes but after the first 20 minutes the e.m.f.-time trace was only followed periodically as another electrode was being tested simultaneously in other cells. From the data given in the appendix it can be seen that the initial decrease in e.m.f. ceased 20 minutes after transfer, and the e.m.f. then remained constant for at least 30 minutes. When it was again recorded after 120 minutes immersion, the e.m.f. was found to be increasing and the final error was 15.4mV. However after the electrode had been transferred back to a standard solution and the transient had died away it was observed that the calibration e.m.f. had also increased by 1.0mV. The e.m.f. variation observed while the glass electrode was placed in the test solution, should strictly speaking be classified as type D_2. However, since the initial decrease in e.m.f. was followed by a long period during which the e.m.f. was constant, and the subsequent increase corresponded exactly to the overall increase in the calibration e.m.f., it seems reasonable to regard this result as a D_1 transient followed by a constant error of 14.4mV.

Two general observations may be made concerning the magnitudes of the transients characterised in tables 7.1 and 7.2. First it may be seen that in several experiments the glass electrode took longer to reach a steady potential in the test solution than after transfer back to a standard solution. This applied particularly to all experiments involving sodium solutions at pH 13 and also for tests of the Pye Ingold electrodes in the lithium solution

of similar pH. Second it was found that the transient observed when one of the electrodes was placed in a lithium solution, died away more rapidly than that observed for the same electrode and the corresponding sodium solution. This was true despite the fact that with the exception of the Pye Ingold all these electrodes gave larger lithium errors than sodium errors.

Some examples will now be cited in illustration of the above comments. Consider first the results obtained with the Jena HA electrode No. 22 at pH 12. With lithium solution (Test 32) this electrode gave an error of 6.2mV and the transient died away in 10 minutes, whereas with sodium solution (Test 18) it gave an error of only 2.6mV but the e.m.f. was still decreasing after 18 minutes. When the Pye Ingold electrode No. 10 was placed in lithium solution of p_wH 12.81 (Test 30) the transient died away in about an hour, but when the electrode was placed in the corresponding sodium solution (p_wH 13.00 Test 29) the transient was still incomplete after 2 hours. Similar results to those just mentioned were obtained with the Pye Ingold electrode No. 15 at pH 13 and with the Radiometer B electrode No. 17 at both pH 12 and pH 13.

When a glass electrode is used to measure the pH of an alkaline solution in which it is known to be in error, it may be necessary, depending upon the accuracy required, to correct the observed reading to allow for the error. In order to make such a correction, it is necessary that the magnitudes of the errors shown by the glass electrode should have previously been determined in solutions of similar cation content and pH, and the glass electrode user may either carry out such a determination himself or rely upon data supplied

by the electrode manufacturer. The accuracy which may be achieved with this correction procedure will depend upon the reproducibility of the errors and this factor has therefore received particular attention here, since the lithia glass electrodes are now widely used for pH measurements.

In order to assess the reproducibility of the alkaline errors it is necessary to take account of their time dependence. A possible approach would be to determine the reproducibility of the error shown by a glass electrode in a particular solution, at some specified time or times after transfer. However in the case of one of these electrodes which gave type D_1 response, it would probably be more convenient for the glass electrode user if the correction procedure outlined above could be based upon the final approximately constant errors calculated in the manner described in section 5.4. The reproducibility of these final errors is determined in the first instance by the precision with which they may be quoted, and this in turn depends upon the constancy of the final e.m.f. for the test solution and any overall change of asymmetry potential. These factors will now be considered.

It has been found, that when one of these glass electrodes which gave type D_1 response, was transferred to a test solution, either the transient died away to give an e.m.f. which was constant to 0.1mV for several minutes, or the rate of change of e.m.f. finally became so slow that the value did not decrease by more than 0.3mV over a period of about 10 minutes or more. This would correspond to a reading constant to 0.01 of a pH unit observed on a pH meter, and hence in these circumstances the e.m.f. will be referred to

as constant to 0.01 of a pH unit. In only a few experiments was the final e.m.f. for the test solution not constant within these limits. However these were in general among the first experiments to be carried out with the lithia glass electrodes in solutions where they gave errors, and it was subsequently realised that in these experiments, the electrodes had not been left in the respective test solutions long enough for this constancy of e.m.f. to be attained. The calibration e.m.f. usually did not change by more than 0.3mV over the period of a test and hence using the procedure described in section 5.4. the final error could in general be quoted with an accuracy of ±0.3mV, that is to the nearest 0.01 of a pH unit.

In some experiments with these electrodes, particularly those involving sodium solution at pH 13, it was observed that even after the electrode had been placed in the test solution for about 40 minutes the e.m.f. was still changing, although the rate of change was usually fairly small. Further experiments were therefore carried out in which the electrodes were left in the respective test solutions for longer periods, sometimes well over an hour, in order to investigate whether the e.m.f. would become constant at some later time. If on the other hand after 40 minutes immersion in a test solution, an electrode gave a final e.m.f. which was observed constant to 0.1mV for several minutes, it was of interest to determine whether the e.m.f. would remain constant if the electrode was left in the solution rather longer. The results of these experiments will now be considered. It will be seen that there usually occurred changes in the calibration e.m.f. and these

reduced the accuracy with which the final errors could be quoted. This was perhaps not surprising since it might be expected that the longer the duration of an experiment the greater the possibility of an overall change of calibration e.m.f. taking place.

Electrode No. 17 was tested twice in 1.0m sodium solution of pH 13 on 14/9/66 (Tests 26 and 27). In the first test (No. 26) the electrode was transferred back to a standard solution after 36 minutes and the steady e.m.f. subsequently obtained showed that there had been no change in the calibration e.m.f. The final error in the test solution was 4.9mV but the e.m.f. was not constant. However it had only changed 0.3mV in the last 15 minutes and hence the error was constant to 0.01 of a pH unit over that time. On repeating the experiment (Test 27) an error of 4.7mV relative to the final e.m.f. in standard solution 1 was observed after 40 minutes but the electrode was then left in the solution for a further 40 minutes. During this time the e.m.f. continued to decrease but the change was only 0.2mV and hence the error was constant to 0.01 of a pH unit over this period. When the electrode was transferred back to a standard solution and the transient had died away, it was found that the calibration e.m.f. showed a small increase on the value observed in standard solution 1. This contributes to the uncertainty in the final error which has therefore been quoted as 4.5 ($\pm$0.3)mV.

Rather similar results were obtained with electrode No. 22 for the same solution on 12/9/66, but in this case the e.m.f. for the test solution became essentially constant after about 30 minutes. In the first experiment (Test 24)

the transient had died away after 35 minutes, giving an error of 4.3mV relative to the final e.m.f. in standard solution 1, and transfer back to a standard solution indicated that there had been very little change in the calibration e.m.f. The experiment was repeated (Test 25) and a constant e.m.f. ($\frac{dE}{dt} = 0$) showing an error of 4.1mV was observed after 30 minutes. The electrode was then left in the solution for a further 70 minutes and during this time the change of e.m.f. was only 0.1mV. However on transferring the glass electrode back to a standard solution and allowing the transient to die away, the calibration e.m.f. was found to have increased by 0.6mV. Taking account of this, the final error has been quoted as 3.7mV which was not in very close agreement with the final error for the first experiment. Also, the precision was $\pm$0.4mV and hence slightly outside the 0.01 of a pH unit level.

For the second test of each of the above pairs, the final error, calculated in the usual way taking account of any change in calibration e.m.f. does not agree with the final error of the first experiment, as well as does the error observed after about 30-40 minutes. This was due, at least in part, to the changes of calibration e.m.f. which occurred during the second experiment in each case. These changes also increased the uncertainty of the final errors. It is possible that if in the second test of each pair (i.e. Tests 26 and 24) the glass electrode had been transferred back to a standard solution earlier, say after about 50 minutes, there would have been no overall change in calibration e.m.f. and the final e.m.f. for

the test solution would not have changed by more than 0.3mV over about 15-20 minutes. The error could then have been quoted to well within the ±0.3mV level of precision and would probably have been in close agreement with that observed in the first experiment of the pair.

Experiments in which the electrodes were left in the test solution for well over an hour were also carried out with the Pye Ingold electrodes (Nos. 10 and 15). Both of these electrodes were tested in sodium solution of p_wH 13.00. Electrode No. 10 was left in the solution for 2 hours (14/9/66 Test 29) and Electrode No. 15 was left in it for 3½ hours (1/11/65 Test 4). In both cases the final e.m.f. for the test solution was still decreasing, although for Electrode No. 10 this change was very slight, and when the electrode was transferred back to a standard solution and the transient had died away, it was found that there had been a small but significant change in the calibration e.m.f. However it was also observed during both experiments, that about 30 minutes after the electrode had been transferred to the test solution, the e.m.f. became constant to 0.01 of a pH unit for 10-15 minutes. Hence, if in each test, the electrode had been transferred back to a standard solution after about 50 minutes in the sodium solution, there might have been very little change in calibration e.m.f. and the final error could probably have been quoted with an accuracy of ±0.3mV.

From the foregoing discussion it may be concluded that the final errors shown by the electrodes which gave type D_1 response in alkaline solutions, probably cannot be expressed with a precision better than ±0.3mV, that is to

the nearest 0.01 of a pH unit. On the basis of the data obtained in this work it would appear that it is not possible to achieve greater precision by leaving the electrodes in the test solutions for long times. However it might be desirable to confirm these conclusions by carrying out further experiments in which glass electrodes would be tested repeatedly in the same solutions, varying the time of immersion from one experiment to another.

In order to express the error shown by one of these electrodes in an alkaline solution, to the above accuracy, the electrode should be left in the test solution for a period, long enough for the e.m.f. to become constant to 0.01 of a pH unit, but not so long that a change in calibration e.m.f. occurs. The length of time required for the e.m.f. observed with the test solution, to attain this constancy, will depend upon various factors such as the type of electrode and the nature of the solution. For example, with an electrode of group 1 in 1.0m sodium solutions it is usually necessary to wait about 20 minutes at pH 13 and about 10 minutes at pH 12. In order to check that the error has become constant to the above level of precision it is then necessary to leave the electrode in the solution for a further period of say 10 or 20 minutes and take a second reading. In fact, as has been seen, the e.m.f. may be constant to 0.01 of a pH unit for a much longer time. Thus in order to obtain an e.m.f. constant to 0.01 of a pH unit using an electrode of group 1 in a sodium solution, it is probably necessary to leave the electrode in the solution for about 40 minutes at pH 13, and 20-30 minutes at pH 12. Once a final e.m.f. for the test solution constant to 0.01 of a

pH unit, has been attained, the glass electrode may be transferred back to a standard solution. If the period for which the electrode was placed in the test solution was not greater than about 50 minutes, any overall change in the calibration e.m.f. will probably be small and the error may then be specified to 0.01 of a pH unit. If a less accurate value is required then shorter times of immersion in the test solution would be adequate.

Having determined the constancy of the final errors shown by these electrodes in alkaline solutions it now remains to examine their reproducibility. The values shown by the various electrodes have been collected together for comparison in tables 7.3 and 7.4. It can be seen that except at pH 13, the errors were very reproducible both for repeated testing of the same electrode and between different electrodes of the same type.

The Pye Ingold were the only electrodes which gave this type D_1 response, that showed errors in the 1.0m sodium and lithium solutions below pH 11. Repeated testing of an electrode in one of these solutions was mainly confined to the same experimental run, but three experiments were carried out, separated by intervals of three and six months, during which Electrode No. 15 was tested in three 1.0m sodium solutions all having a p_wH of about 10.5. A small increase in the error was noted in the third experiment and this was probably due to aging of the glass electrode rather than the small increase in p_wH. Nevertheless the variation of the error over all three experiments was only 0.6mV.

Repeated testing of an electrode in the sodium and lithium solutions of

TABLE 7.3.

Errors of Lithia Glass Electrodes in 1.0m Sodium Solutions

Beckman E2 Electrodes.

p_wH	Electrode No. 3			Electrode No. 19		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
10.52				22/11/65	-	0.0
11.97	25/11/65	72	+1.5	22/11/65	20	+1.4
				22/11/65	21	+1.6
13.00	25/11/65	73	+3.1	12/11/65	74	+2.6

Electrode No. 18 - E.I.L. GHS 33

p_wH	Date	Test	Error (mV.)
10.52	18/11/65	-	0.0
	25/11/65	-	0.0
11.97	25/11/65	22	+1.0
13.00	25/11/65	23	+2.9

TABLE 7.3. (Cont.)

Jena HA Electrodes

p_wH	Electrode No. 22			Electrode No. 29		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.16	3/8/66	-	0.0			
	10/8/66	-	0.0			
10.52	25/11/65	17	+0.6			
11.97	25/11/65	18	+2.6			
13.00	25/11/65	19	+5.4	15/9/66	46	+3.0
	12/ 9/66	24	+4.2			
	12/ 9/66	25	+3.7			

Radiometer B Electrodes

p_wH	Electrode No. 4			Electrode No. 17		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
10.52	22/11/65	-	0.0	18/11/65	-	0.0
10.55				5/5/66	71	+0.5
11.97	22/11/65	12	+1.6	18/11/65	6	+1.5
				18/11/65	8	+1.3
13.00	22/11/65	13	+3.4	1/11/65	2	+4.6
				18/11/65	7	+4.0
				14/9/66	26	+4.9
				14/9/66	27	+4.5

TABLE 7.3. (Cont.)

Pye Ingold Electrodes

p_wH	Electrode No. 10			Electrode No. 15		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.16				12/8/66	376	+0.5
9.85	30/7/65	64	+0.8	4/8/65	66	+1.0
10.04				1/11/65	5	+1.3
10.49	4/8/65	65	+2.1			
	5/8/65	68	+2.0	4/8/65	67	+1.9
10.52				22/11/65	14	+2.0
10.55				5/5/66	39	+2.5
11.97				22/11/65	15	+10.7
				22/11/65	16	+10.4
13.00	14/9/66	29	+26.1 ±0.5	1/11/65	4	+24.0

TABLE 7.4.

Errors of Lithia Glass Electrodes in 1.0m Lithium Solutions

p_wH	Radiometer 8 Electrode No. 17			Jena HA Electrode No. 22		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.56	18/8/65	-	0.0			
10.20				11/5/66	34	+0.1
10.59	18/8/65	373	+0.5			
	18/8/65	374	+0.4			
	18/8/65	375	+0.6			
11.81	27/5/66	35	+5.2	11/5/66	32	+6.2
	27/5/66	36	+5.4			
12.81	5/5/66	31	+16.6	11/5/66	33	+20.4
	14/9/66	28	+14.4			

Pye Ingold Electrodes

p_wH	Electrode No. 10			Electrode No. 15		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.56				24/8/65	-	0.0
10.59				19/8/65	261	+0.9
				24/8/65	262	+0.9
11.81				27/5/66	37	+8.0
12.81	14/9/66	30	+24.4	5/5/66	38	+26.5

pH 12, always took place on the same day whereas duplicate experiments for the solutions of pH 13 were carried out not only on the same day but also separated by long intervals of up to several months. This is probably one of the reasons for the poor reproducibility of the errors at pH 13, since the reproducibility of the errors shown by electrodes over long periods is likely to depend upon the individual electrode and the treatment it receives. The influence of these factors upon the results obtained with two of the electrodes tested here will be considered in the next paragraph. The poor reproducibility observed for repeated testing of an electrode in a solution of pH 13 on the same day, has already been discussed.

The error shown by the Radiometer B electrode No. 17 was observed to decrease between the 1st and 8th of November 1965, but had increased again when the electrode was tested in the same solution almost a year later (14/9/66). It may be significant that the decrease in the error coincided with a discontinuity in the slow increase in calibration e.m.f. observed for the electrode as it became older. As will be seen in chapter 9, Jena HA Electrode No. 22 was tested in a fluoride solution between the two dates upon which it was tested in the sodium solution at p_wH 13, and this may account for the observed decrease in the alkaline error.

7.2. Corning Electrodes

Comparatively few tests were carried out with the Corning electrodes

since they were not available until just before the end of the work. However results were obtained for two electrodes in 1.0m sodium solution of p_wH 13.00 and for one of these electrodes (No. 27) in 1.0m lithium solutions. When tested in the sodium solution, both electrodes gave type D_1 e.m.f.-time variations similar to those already considered in the last section but a somewhat different response was shown by Electrode No. 27 in the lithium solutions.

The data for experiments involving the sodium solution are presented in table 7.5 in a manner similar to that used earlier for the other lithia glass electrodes which gave the same type of response. Since several experiments were carried out with this solution, it is possible to consider the reproducibility of the final error over the short period of time involved. In each experiment, the transient observed when the electrode was placed in the sodium solution itself, died away fairly rapidly and was complete well before the electrode was transferred back to a standard solution. It was found that the e.m.f. for the test solution never changed by more than 0.1mV during the period after the end of the transient, which was sometimes as long as 15 or 20 minutes. Hence this final e.m.f. was constant to well within the $\pm$0.3mV level of precision.

During each of these experiments changes of calibration e.m.f. occurred, and the contribution to the uncertainty in the final error from this source, was probably greater for the Corning electrodes than for any other type of lithia glass electrode tested. The change in calibration e.m.f. (ΔE_7) and

TABLE 7.5.

Transients and Errors shown by Corning Electrodes

Experiments with 1.0m Sodium Solution p_wH 13.00

ΔE, ΔE_7, E_T and E_S all in mV. t_T and t_S in minutes

	Date	Test	ΔE	E_T	t_T	E_S	t_S	ΔE_7
Electrode No. 27	12/9/66	41	3.3(±0.4)	1.1	5	1.5	3	+0.6
	12/9/66	42	2.2(±0.1)	1.8	10	1.8	4	+0.2
	15/9/66	44	2.3(±0.4)	3.3	5	2.5	3	+0.7
	15/9/66	45	2.3(±0.2)	1.2	5	1.5	5	+0.4
Electrode No. 30	12/9/66	43	1.8(±0.3)	5.7	30	2.2	8	-0.4

TABLE 7.6.

Transients and Errors shown by Corning Electrode No. 27

Experiments with 1.0m Lithium Solution

ΔE_x, ΔE_y, ΔE_7, E_A, E_B and E_S all in mV. t_A, t_B and t_S in minutes

p_wH	Date	Test	ΔE_x	ΔE_y	E_A	t_A	E_B	t_B	E_S	t_S	ΔE_7
11.81	27/5/66	47	+11.1	+11.6	1.0	4	2.2	31	3.7	5	+1.7
	27/5/66	48	+12.8	+13.7	1.8*	4	1.9	28	2.9*	4	+1.0
12.81	12/9/66	40	+27.7	+28.5	3.0	5	6.0	65	4.3	6	+5.2

the uncertainty of the final error are given in table 7.5 for each experiment. It can be seen that in two cases the change in calibration e.m.f. amounted to 0.6mV or more, which would correspond to a change of 0.01 of a pH unit in the calibration reading observed on a pH meter. Taken as a whole therefore, the uncertainty of the final errors shown by the Corning electrodes in this sodium solution, was greater than ±0.3mV, although in some cases the errors could be quoted to within this level of precision.

It is now possible, having considered the accuracy of these errors, to examine their reproducibility. It may be seen from table 7.5, that except for test 41 with Electrode No. 27, the reproducibility of the errors was in fact comparable with their precision. The reason for the exceptionally large error observed in test 41 is not known, but it may possibly have been due to the fact that the experiment was carried out immediately after the electrode had been tested in 1.0m lithium solution of p_wH 12.81 (Test 40).

The type of response observed when Electrode No. 27 was tested in alkaline solutions containing lithium ions, is shown in figure 23. A type D_2 e.m.f.-time curve was observed with the test solution and in each case a significant increase in calibration e.m.f. also occurred. The initial decrease in e.m.f. (E_A) observed immediately after the electrode was transferred to the lithium solution itself, was fairly small and lasted only a few minutes. The subsequent increase (E_B) took place relatively slowly and this portion of the trace was almost linear. In each test the e.m.f. was still increasing

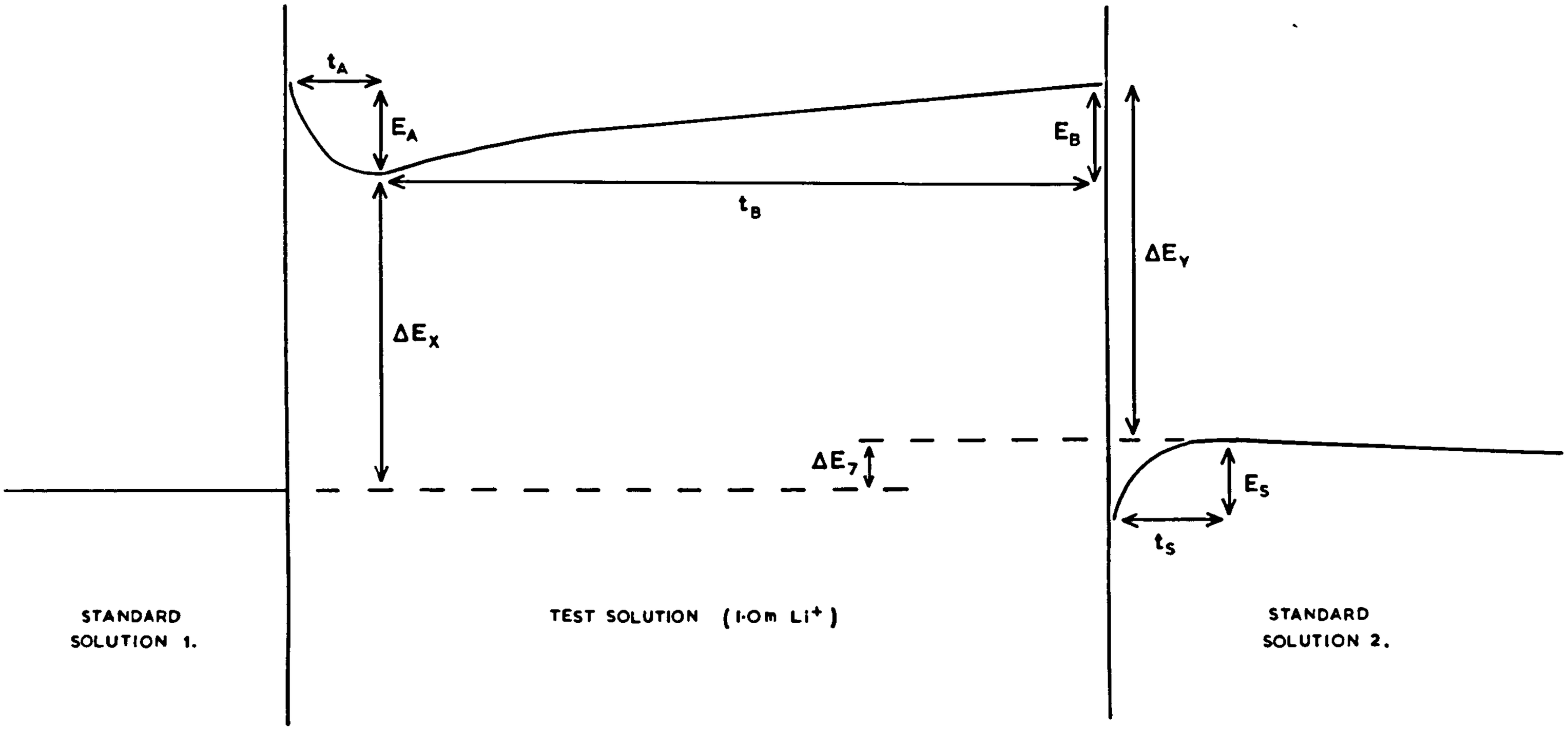


Fig. 23 The Response of Corning Electrode No. 27 – Lithium Errors

when the electrode was transferred back to a standard solution. The e.m.f. for the standard solution showed an initial rapid increase which was followed by a constant value or a very slight decrease.

The errors and transients obtained with this electrode in these experiments with lithium solutions are presented in table 7.6. It was considered desirable for these experiments to quote two errors, which have been termed ΔE_x and ΔE_y, and are shown in figure 23. ΔE_x was taken as the difference between the minimum e.m.f. observed for the lithium solution and the final e.m.f. for standard solution 1, whereas ΔE_y is the difference between the final e.m.f. observed with the lithium solution and the e.m.f. after the transient for standard solution 2. If the latter was not constant, the error is given relative to the maximum of the e.m.f.-time curve for this solution. The stated change in the calibration e.m.f. (ΔE_7), is the difference between the final e.m.f. for standard solution 1 and the constant or maximum e.m.f. for standard solution 2. Two experiments were carried out with the solution of p_wH 11.81 and it may be seen from the appendix, that the reproducibility of the error was poor at all points on the e.m.f.-time curves.

7.3. Radiometer C Electrodes

When a Radiometer C electrode was placed in an alkaline solution containing sodium ions, the transient observed was usually small and of short duration, and hence the e.m.f. rapidly attained an approximately constant

value. In fact, in some experiments there was no transient at all and the e.m.f. was approximately constant from immediately after transferring the glass electrode to the solution. Hence the most prominent aspect of the e.m.f.-time traces obtained during these experiments, was the zero, or slight and approximately linear change denoted as feature E. However when describing these e.m.f.-time traces in terms of the main features discussed in section 5.4., it is necessary to remember the stipulation that feature E, like feature B, should commence not more than about 3 minutes after transfer of a glass electrode to a new solution. This was to make it possible to extrapolate the linear change back to the instant of transfer, since feature E was distinguished from feature B by the fact that only the latter indicated negligible instantaneous error.

In only a very small number of experiments was a transient lasting more than three minutes observed after a Radiometer C electrode was transferred to an alkaline sodium solution, and these transients were all of type D_1. The transients of less than three minutes duration were either of type C_1 or D_1 and hence the e.m.f.-time curves could be described in one of the following ways

1. No transient - E
2. Transient lasting no more than 3 minutes - $D_1 + E$ or $C_1 + E$
3. Transient lasting more than 3 minutes - D_1

When one of these Radiometer C electrodes was transferred from an alkaline sodium solution in which it gave an error, back to a standard solution, a

type D_1 transient was almost invariably observed. These transients were rather larger than those observed after transfer to the sodium solution itself and were comparable in size to those observed with the other lithia glass electrodes in similar circumstances. They usually lasted for well over three minutes and hence the e.m.f.-time curves have been described as D_1 rather than $D_1 + E$.

When a Radiometer C electrode was tested in an alkaline solution containing lithium ions it responded in the manner shown in figure 24, except for a few experiments with Electrode No. 7 in which the errors were fairly small. Apart from these exceptions, the electrodes gave type C_1 response in the lithium solution - with an e.m.f. variation which increased with the magnitude of the error - and type D_1 response on being transferred back to a standard solution. Electrode No. 16 always showed an overall increase in the calibration e.m.f. (E_7) after testing in an alkaline lithium solution, although this was small at p_wH 10.59. However in the corresponding tests with Electrode No. 7 the calibration e.m.f. always remained effectively constant.

The results of the experiments with these two electrodes and the alkaline lithium solutions are summarised in table 7.8. If the C_1 transient observed for the test solution, was incomplete when the electrode was transferred back to a standard solution, the time quoted is the total time for which the electrode was placed in the lithium solution. The value is then underlined. Also in table 7.8, as with earlier tables in this chapter, where the details

TABLE 7.7. Transients and Errors shown by Radiometer C Electrodes

Experiments with 1.0m Sodium Solutions

Electrode No. 7

p_wH	Date	Test	Error (mV.)	Test Solution Response	Transient		Standard Solution	
					mV.	min.	mV.	min.
8.83	2/6/64	369	+0.9	D_1 + E	0.9	1	3.0	9
9.14	9/8/66	380	+1.2	E			2.6 (C_1 + E)	1
9.16	9/8/66	381	+1.3	C_1 + E	1.4	1	-	-
9.85	10/8/65	61	+2.6	C_1 + E	0.8	2	2.5	9
	10/8/65	62	+2.6	C_1 + E	0.5	1	1.1	6
10.49	10/8/65	63	+5.4	D_1	1.1	4	1.4	10

Electrode No. 16

p_wH	Date	Test	Error (mV.)	Test Solution Response	Transient		Standard Solution	
					mV.	min.	mV.	min.
9.14	9/8/66	58	+1.7	C_1 + E	0.3	2	1.9	8
9.16	3/8/66	69	+1.5	E*			1.7[x]	5
	3/8/66	70	+1.7	D_1 + E	1.2[x]	2	1.5[x]	7
9.85	10/8/65	59	+3.0	E			1.5	5
10.49	10/8/65	60	+5.8	D_1 + E	0.6	3	1.2	5
10.52	18/11/65	9	+6.1	E			1.4	6
10.55	5/5/66	56	+7.1	D_1 + E	0.6	2	0.9	8
11.97	18/11/65	10	+22.1	D_1 + E	0.4	2	3.8	15
	18/11/65	11	+22.6	D_1	1.0	6	4.5	19

[x] Transfer to or from an acetate buffer as standard solution.

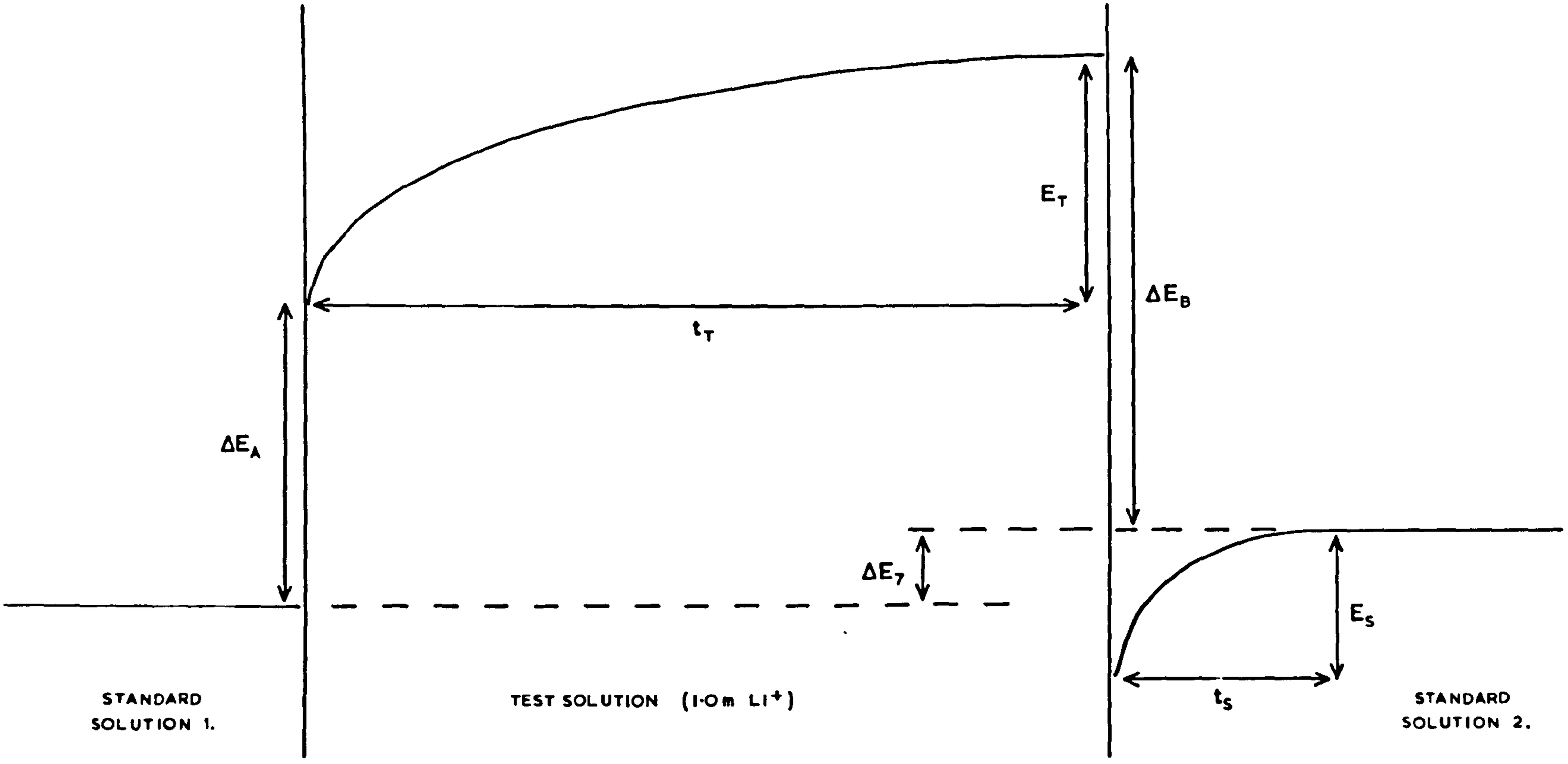


Fig. 24 The Response of Radiometer C Electrodes — Lithium Errors

TABLE 7.8. Transients and Errors shown by Radiometer C Electrodes

Experiments with 1.0m Lithium Solutions

Electrode No. 7

Changes of calibration e.m.f. were always small with this electrode.

p_wH	Date	Test	Error (mV.)	Test Solution Response	mV.	min.	Standard Solution Response	mV.	min.
8.48	6/8/64	-	0.0						
9.27	6/8/64	370	+0.6	C_1	2.9	8	D_1	0.6	5
	6/8/64	371	+0.6	C_1	1.6	14	C_1 + E	5±1	2
	6/8/64	372	+0.6	D_1 + E	0.5	1	C_1 + E	4±1	2
10.20	11/5/66	53	+1.9	D_1 + E	1.2	1	D_1	0.5[x]	4
10.59	10/8/65	55	+2.9	C_1	0.6	17	D_1	0.8	6
11.81	11/5/66	52	+18.3	C_1	3.9	26	D_1	1.5	12

Electrode No. 16 Symbols corresoond to figure 24

ΔE_A, ΔE_B, E_T, E_S and ΔE_7 all in mV. t_T and t_S in minutes.

p_wH	Date	Test	ΔE_A	ΔE_B	E_T	t_T	E_S	t_S	ΔE_7
10.59	10/8/65	54	+3.8	+4.6	1.1	40	1.1	3	0.3
11.81	27/5/66	49	+17.2	+22.9	7.0	84	2.0*	10	1.3
12.81	5/5/66	50	+40.2	+49.5	10.6	102	5.2	25	1.3
	12/9/66	51	+47.1	+57.2	11.6	126	2.7	10	1.5

[x] In describing this transient as type D_1 a very rapid initial decrease of e.m.f. (0.8mV.) has been neglected.

of the response shown by an electrode after a transfer, are marked with an asterisk, the electrode was transferred either to or from an acid standard solution. For Electrode No. 16 it was not possible, except at p_wH 10.59 (Test 54), to state the final errors with a precision of ±0.3mV, on account of the changes of calibration e.m.f. which occurred. Hence for all the experiments with this electrode two errors have been quoted, namely ΔE_A and ΔE_B as indicated in figure 24.

As with the other lithia glass electrodes the question of the reproducibility of the errors has received attention here. For the sodium solutions this question has been investigated with reference to the approximately constant final errors calculated according to the procedure outlined in section 5.4. As before, the first stage was to determine the precision with which these errors may be specified, and in these experiments this was facilitated by the short duration of the transients.

When a Radiometer C electrode was transferred to an alkaline solution containing sodium ions, the e.m.f. rapidly attained a steady value and was usually observed to be constant to 0.01 of a pH unit for a period of about 10 minutes or more. Indeed the e.m.f. was often constant to 0.1mV for several minutes. Since these electrodes in general reached an approximately constant e.m.f. in an alkaline sodium solution, more rapidly than did the other lithia glass electrodes, the experiments were of relatively short duration and this factor would probably tend to keep any changes of calibration e.m.f. to a minimum. In fact the calibration e.m.f. usually did not change by more than

0.3mV over the duration of an experiment and hence the errors shown by the approximately constant final e.m.f.'s could be quoted with an accuracy well within ±0.3mV.

Some results of duplicate experiments with the same solutions are to be found in table 7.7 and these include both repeated testing of the same electrode and experiments with the two different electrodes of this type. It can be seen that the errors were not always reproducible to 0.01 of a pH unit (±0.3mV) but the reproducibility was nevertheless fairly good. The errors observed on repeated testing of one electrode in the same solution during a single experimental run, however, usually agreed with each other to within 0.3mV. The only exception was the pair of experiments for Electrode No. 16 with the solution of p_wH 11.97, but since the errors observed with this solution were over 20mV, this was perhaps not surprising.

Some experiments which indicate the reproducibility of the error in sodium solution over longer periods of time, were carried out with Electrode No. 16. This electrode was tested in three 1.0m sodium solutions all having a p_wH of about 10.5 and the tests (Nos. 9, 56 and 60) were separated by periods of three and six months. It may be seen from table 7.7 that the error increased by over 1mV between the first and third of the experiments. However it should be remembered that the experiments were carried out using the solutions in the order of increasing p_wH and this factor may have been partly responsible for the increase in the error. Nevertheless it would appear that the error does increase slightly as the electrode becomes older, since the

observed increase was probably too large to be accounted for entirely by the rise in p_wH.

Consideration of the reproducibility of the errors shown by these Radiometer C electrodes in alkaline lithium solutions, has been somewhat restricted by the limited amount of data obtained in the time available. The only examples of repeated testing of one electrode in the same solution were for Electrode No. 7 with the solution of p_wH 9.27, and Electrode No. 16 at p_wH 12.81. The errors shown by Electrode No. 7 at p_wH 9.27 were small and consequently very reproducible. On the other hand, the errors shown by Electrode No. 16 at p_wH 12.81, were fairly large and as might therefore be expected were not in close agreement. As has been seen, during these experiments with Electrode No. 16, there occurred changes of over 1mV in the calibration e.m.f. and hence it was not possible to specify the final errors with great precision. Also, the e.m.f. observed while the electrode was placed in the lithium solution, did not reach a steady value even after times of well over an hour.

For the lithium solutions of lower pH, the agreement between the final errors shown by the two electrodes was poor and not as good as between the errors observed with the sodium solutions of similar pH. Possibly more reproducible results would be obtained for lithium solutions of pH below about 11.0 or 11.5, on repeated testing of a single Radiometer C electrode, but further experiments are required in order to test this. Although the reproducibility of the final errors shown by these electrodes in alkaline

solutions containing lithium ions, was in general poor, no significant improvement could be obtained by considering the errors at other points on the e.m.f.-time curves.

7.4. Relative Magnitudes of the Alkaline Errors of Lithia Glass Electrodes

Two objects of the present work have been first, the reinvestigation of the relative magnitudes of the errors, shown by lithia glass electrodes in alkaline solutions containing sodium or lithium ions, and second the comparison of the magnitudes of the alkaline errors shown by the different types of electrode. In order to make a definite statement concerning the relative magnitudes of the errors shown, either by the same glass electrode with different solutions, or by different glass electrodes in the same solution, it is strictly speaking insufficient to make single measurements of the errors, since some knowledge of their reproducibility is also required. This is true irrespective of whether the experiments are all carried out within a few hours of each other on the same day or are separated by longer periods, perhaps several months. When comparing the errors of individual electrodes in different solutions, this consideration applies not only for solutions containing different cations, which are of particular interest here, but also to solutions containing the same cation at different concentrations and pH values. Hence before it is possible to say, that the error shown by an electrode in solutions of a given cation, increases with the cation

concentration and pH, it is necessary to have checked that the errors are fairly reproducible. The reproducibility of the alkaline errors of these lithia glass electrodes has been considered when presenting the data, and it is therefore now possible to examine their relative magnitudes and hence demonstrate how the electrodes were divided into two groups on this basis.

It has been seen that in general, any variations in the magnitudes of the errors shown by the lithia glass electrodes in alkaline solutions, were small relative to the errors themselves. This was true both for repeated testing of an electrode during a single experimental run and also over much longer periods of time. Apart from the few exceptions which have been mentioned, the reproducibility of the errors was particularly good for repeated testing of an electrode on the same day. On the other hand the reproducibility over periods of several months, probably depends upon the individual electrode and the treatment it receives. Hence in order to determine the relative magnitudes of the errors shown by a glass electrode in various solutions it is probably sufficient, provided the magnitudes of the errors are not too close, to test the glass electrode once in each solution on the same day. However if the experiments with the different solutions are spread out over a period of several months, it is desirable to have some information concerning the reproducibility of the errors shown by the electrode over that time. These considerations will be taken into account when discussing the errors shown by the various electrodes.

There could be no doubt that the Corning, Jena HA and Radiometer B

electrodes gave much larger errors in 1.0m lithium solution than in sodium solution of the same concentration and pH. For example, the Radiometer 8 electrode No. 17 gave errors of 4.6, 4.0, 4.9 and 4.5mV during different experiments with 1.0m sodium solution of p_wH 13.00. In 1.0m lithium solution of p_wH 12.81 it showed errors of 16.6 and 14.4mV and thus it is quite clear that the lithium error of this electrode is larger than the error in sodium solution. Similarly it is clear that the lithium error (20.4mV) of the Jena HA Electrode No. 22 at pH 13 is larger than the sodium error (5.4, 4.2 and 3.7mV). Despite the fact that the reproducibility of the errors shown by the Corning electrode No. 27, was in general not as good as for the two electrodes just considered, there was again no doubt that the lithium error was larger than the sodium error. In fact this electrode gave larger lithium errors and smaller sodium errors than any other electrode tested.

Although these conclusions are based upon the approximately constant final errors observed with these electrodes, they nevertheless remain valid when one takes into account the time dependence of the e.m.f. during these experiments. When one of these electrodes was placed in an alkaline sodium solution, type D_1 response was observed and hence the largest error was that indicated by the initial e.m.f. However in none of the experiments with sodium solutions mentioned above, was the initial error larger than the minimum error observed during the corresponding experiment or experiments with lithium solution of the same concentration, and pH. The largest initial error observed when Electrode No. 17 was placed in 1.0m sodium solution was 9.7mV

(Test 27) and even this was significantly smaller than the minimum errors observed during the corresponding experiments with lithium solution. Similarly the largest initial error observed for Electrode No. 22 when tested in the same sodium solution was 12.1mV (Test 19) which was again smaller than the 20.4mV lithium error.

For the Pye Ingold and Radiometer C electrodes it was not clear whether the error for a solution containing lithium ions was larger than that for a sodium solution of similar concentration and pH since they were of comparable magnitude. Both Pye Ingold electrodes were tested in sodium and lithium solutions of pH 13 but for neither of the two electrodes was the reproducibility of the errors checked for this high pH. Electrode No. 10 was tested in both solutions on the same day but since the errors were well over 20mV their reproducibility is doubtful even over such a short time. At this pH, Electrode No. 10 showed a larger error in the sodium solution than in the lithium solution but with Electrode No. 15 the position was reversed and the lithium error was larger. Electrode No. 15 was tested in both sodium and lithium solutions at pH 12, but the experiments were separated by several months and no evidence was obtained for the reproducibility of the errors shown by Electrode No. 15 at this pH over so long a time. In fact the evidence for the reproducibility of the errors shown by the Pye Ingold electrodes was obtained mainly with solutions having pH below 11 for which the errors were not very large.

The two Radiometer C electrodes were tested in 1.0m sodium and lithium

solutions of pH 10.5 on the same day (10/8/65) and both showed a somewhat larger error in the sodium solution than in the lithium solution. This was despite the fact that the latter was of slightly higher pH. Electrode No. 16 was also tested in both sodium and lithium solutions of pH 12 but here it was not possible to say which error was the larger since they were of comparable size and the experiments were separated by several months.

It is also possible to reach definite conclusions concerning the errors shown by different electrodes in the same solution or solutions. This was particularly true for the sodium solutions for which the magnitudes of the errors were spread over a greater range than for the lithium solutions. The errors shown by the Beckman E2, Corning, E.I.L. GHS 33, Jena HA and Radiometer B electrodes in sodium solutions were of about the same size. It is thus not possible to make any statement concerning their relative magnitudes except that the errors of the Corning electrodes were perhaps slightly smaller than those shown by the electrodes of the other four types. It is quite clear however that all these types of electrode gave much smaller errors in sodium solutions than the Pye Ingold and Radiometer C electrodes which gave errors in the 1.0m sodium solutions employed, at a pH well below 11. The first five electrodes listed above were therefore regarded as group 1 and the Pye Ingold and Radiometer C electrodes as group 2. It has also been seen that the Corning, Jena HA and Radiometer B electrodes from group 1 gave much larger errors in 1.0m lithium solution than in the sodium solution of the same pH whereas the sodium and lithium errors of the group 2 electrodes were of about

the same magnitude.

These conclusions concerning the relative magnitudes of the sodium and lithium errors of lithia glass electrodes will be compared with those of previous investigations, in chapter 11. In only one previous investigation was the time dependence of the alkaline errors of glass electrodes considered and the types of e.m.f.-time variations observed in that work will be compared with those observed here for electrodes of the same type. The errors shown by the electrodes tested in this work will be compared with the values predicted by the manufacturers and some further comments will be made concerning the use of these electrodes for pH measurements with alkaline solutions.

CHAPTER 8.

Alkaline Errors shown by Soda Glass Electrodes

As has already been stated, two types of soda glass electrode were tested in this work, the E.I.L. GG 33 and the Jena H, and these gave errors in molal sodium solutions at a lower pH than any of the lithia glass electrodes tested, the Jena H showing smaller errors than the GG 33. Both types of electrode were also tested in molal lithium solutions and the GG 33 electrodes were also tested in molal potassium solutions, the magnitudes of the errors being in the order $Na^+ > Li^+ > K^+$ at any given pH. It was found from experiments with the type GG 33, that in the pH range under investigation the electrodes were not affected by the anions in solution. Thus, as shown by the data given in table 8.1, electrode No. 1 gave error-free behaviour in buffers containing 0.4 and 1.0m $MgCl_2$ (i.e. Cl^- molality of 0.8 and 2.0) and as will be seen later in this chapter, the electrodes which were tested in solutions of potassium salts gave the same behaviour in solutions of KBr as in solutions of KCl.

The magnitudes of the errors shown by the GG 33 electrodes in 1 molal sodium solutions under normal conditions are given in table 8.2. It may be recalled that during the early part of the present work, 0.1m HCl was used as a standard solution and that it was later abandoned in favour of 0.1m H_2SO_4 since, as the soda glass electrodes became older, they began to show small negative errors in the HCl. However, the only data from experimental runs involving 0.1m HCl as standard solution, which have been included in table 8.2,

TABLE 8.1.

Electrode No. 1.

14/8/63

Initial Solution 0.1m HCl

(E.I.L. GG 33 - Stem not waxed)

Final e.m.f. 0.3965
(Constant 10 min.)

Solution	0.1mCl^-/T 1.1m $MgCl_2$ p_wH 9.11	0.1m HCl	0.1mCl^-/T 1.1m $MgCl_2$ p_wH 9.11	0.1m HCl	0.1mCl^-/T p_wH 7.65	0.1mCl^-/T 0.4m $MgCl_2$ p_wH 8.45	0.1mCl^-/T p_wH 7.65
Time (min.)							
0	0.3966	0.3962	0.3966	0.3959	0.3962	0.3962	0.3963
1	0.3966	0.3964	0.3966	0.3963	0.3965	0.3964	0.3965
2	0.3966	0.3964	0.3966	0.3964	0.3965	0.3964	0.3965
5	0.3965	0.3964	0.3965	0.3964	0.3965	0.3964	0.3965
10	0.3965			0.3964	0.3965	0.3964	0.3965
Final	0.3965 (10)	0.3964 (5)	0.3965 (9)	0.3964 (15)	0.3965 (14)	0.3964 (15)	0.3965 (15)
ΔE(mV)	+0.1	-0.1	+0.2	-0.2	+0.1	-0.1	+0.1
Response	B	B	B	A + B	A + B	B	B

TABLE 8.2.

Errors of E.I.L. GG 33 Electrodes in 1.0m Sodium Solutions.

p_wH	Electrode No. 1			Electrode No. 5			Electrode No. 6		
	Date	Test	Error (mV)	Date	Test	Error (mV)	Date	Test	Error (mV)
8.43	11/6/64	255	+1.4	11/6/64	257	+1.1	11/6/64	253	+1.2
8.83	17/5/65	84	+2.1	2/6/64	252	+1.7	19/5/65	90	+1.7
	17/5/65	85	+2.2	11/5/65	79	+1.3	19/5/65	91	+1.8
9.84				21/12/65	185	+6.3			
				29/7/65	127	+6.2	11/8/65	140	+6.1
				11/8/65	146	+6.8			
10.49	29/7/65	123	+15.2	29/7/65	128	+15.0	11/8/65	142	+15.4
				11/8/65	147	+15.8			
				11/8/65	149	+15.9			
10.55	6/5/66	377	+18.0	6/5/66	215	+17.7			
				6/5/66	216	+17.9			

TABLE 8.2. (Cont.)

p_wH	Electrode No. 8			Electrode No. 12			Electrode No. 14		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)	Date	Test	Error (mV.)
8.43	11/6/64	259	+0.7	22/7/64	328	+1.5			
	18/6/64	275	+0.7	22/7/64	329	+1.6			
	9/7/64	289	+0.6						
	22/7/64	323	+0.7						
8.83	28/5/64	242	+1.0				11/5/65	353	+1.0
	2/6/64	247	+1.2				19/5/65	355	+1.2
	11/5/65	75	+1.1				21/5/65	357	+1.1
9.14				10/8/66	225	+3.1			
				10/8/66	228	+3.3			
9.16	3/8/66	218	+2.0	10/8/66	226	+3.1			
				10/8/66	227	+3.2			
9.84				21/12/65	179	+8.0			
9.85	10/8/65	136	+5.4						
	10/8/65	139	+5.4						
10.04				4/11/65	156	+9.3			
				12/11/65	161	+10.1			
10.49	10/8/65	137	+13.0						
10.55	5/5/66	213	+16.0						
13.00				4/11/65	157	+107			

were obtained before these errors in the HCl appeared. That is to say, they were obtained during experimental runs when error-free transfers between 0.1m HCl and a tris buffer were also observed for the glass electrode in question. Nevertheless 0.1m was clearly the maximum possible HCl concentration before the negative errors set in and this solution may therefore have had some influence upon the response of the electrodes in alkaline solutions even before the error in the 0.1m HCl appeared. However, since the alkaline errors observed during the early experimental runs were all fairly small, any increase in the magnitude of the error, above that which would be observed in the absence of any HCl solution, would probably be almost negligible.

Since soda glass electrodes are not used a great deal nowadays the question of the precision and reproducibility of their errors will not be considered in detail as it was for the lithia glass electrodes. However from considerations similar to those discussed in the last chapter, it may be concluded that the precision of the final errors shown by the soda glass electrodes in alkaline solutions, is in general also about ±0.3mV. Furthermore as can be seen from table 8.2, the magnitudes of the final errors shown by an electrode in a given solution were fairly reproducible. This was particularly true within the period of one experimental run but in some cases good agreement was obtained between tests separated by several months. The increase in the errors shown by electrode No. 5 at p_wH's 9.85 and 10.49 between 29/7/65 and 11/8/65 was probably due to the fact that the electrode was tested in 1.0m HCl on the earlier date. This is supported by the fact that the error shown by

the electrode at p_wH 9.84 on 21/12/65 was in good agreement with the earlier value. Also the increase in the error shown by electrode No. 12 between the 4th and 12th November 1965 for the solution of p_wH 10.04 can probably be accounted for in the same way.

Nevertheless there is evidence to suggest that the errors increase slowly as the electrode becomes older. For example, the difference between the errors shown by electrode No. 8 at p_wH 10.49 on 10/8/65 and at p_wH 10.55 on 5/5/66, is too large to be accounted for by the small difference in p_wH, and it will be seen that further evidence for this is provided by the errors observed with potassium solutions to be presented later in the chapter. However, for an electrode of this type, the age, or time after first soaking it in water, was apparently not the only factor which determined the magnitude of the error shown in a given solution. For example as may be seen from figure 25, electrode No. 8 gave consistently lower errors than electrode No. 12 which was the newer electrode. Figure 25 also shows that the errors observed for the different E.I.L. GG 33 electrodes during experiments with sodium solutions were in fairly close agreement.

When the GG 33 electrodes were tested in 1.0m sodium solutions under normal conditions, e.m.f.-time variations of types D_1, D_2 and C_1 were observed. The type D_2 response took the form of an initial rapid decrease in the error followed by a drift of e.m.f. during which the error increased. The C_1 response appeared to be a special form of the type D_2 described above in which the initial decrease in error was absent. Similarly the D_1 might be regarded

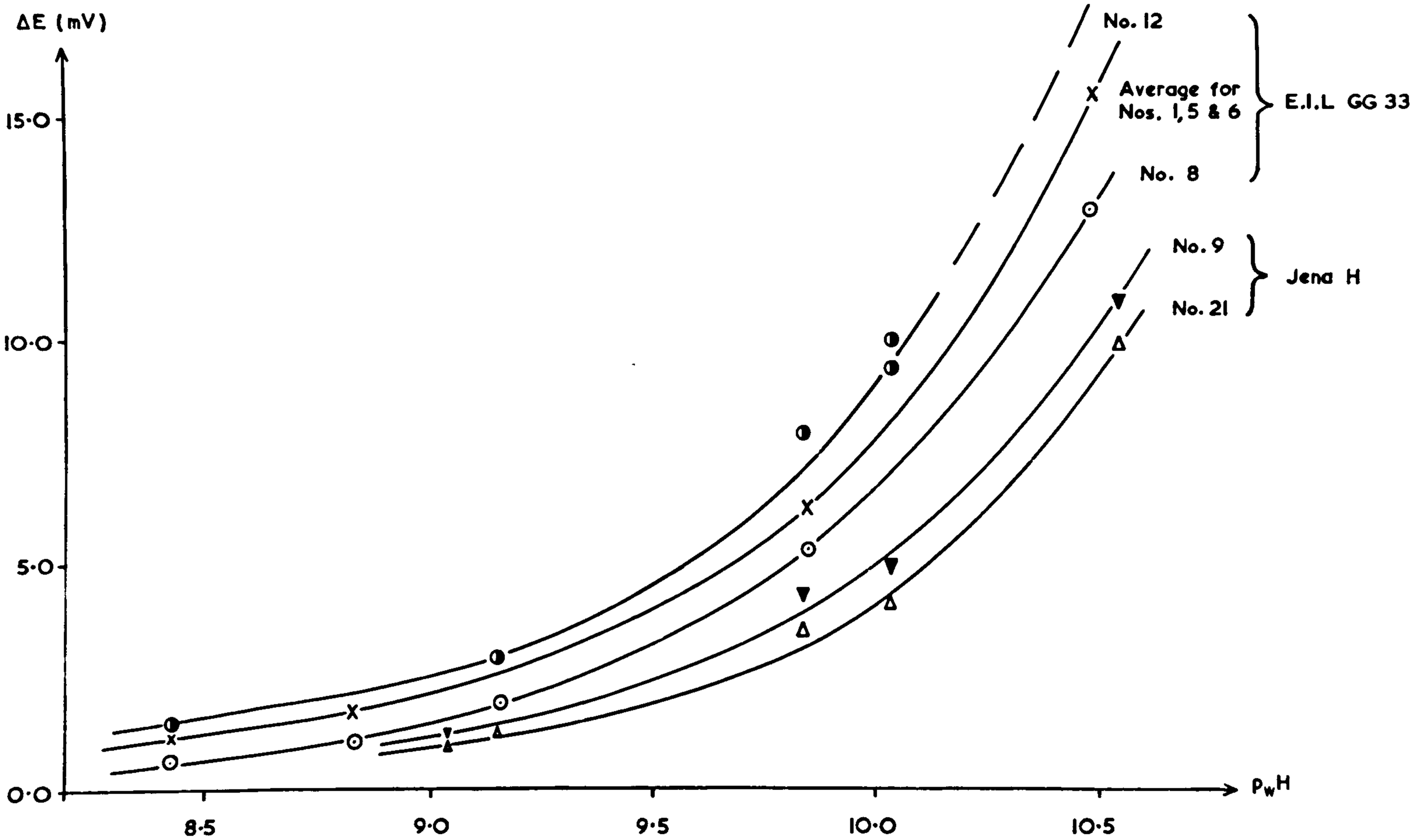


Fig. 25 The Errors of Soda Glass Electrodes in 1·0m Na^+ Solutions.

as a form of type D_2 in which the initial decrease in error predominated to the extent that the subsequent increase was not observed. These three possibilities are shown in figure 26.

The transients shown by the GG 33 electrodes when tested in sodium solutions have been characterised by listing in table 8.3, the e.m.f. variations E_1, E_2, E_3 and E_4 and the corresponding times t_1, t_2, t_3 and t_4 indicated in figure 26. If one determines the number of each type of response among the 43 experiments in table 8.3, the following result is obtained:-

Response	Test Solution	Standard Solution 2
C_1	20	4
D_2	14	2
D_1	2	31
E	7	6

It can be seen that D_1 response was rarely observed for the sodium test solution but was frequently observed when an electrode was transferred back to a standard solution. For electrodes Nos. 1, 8 and 12, if an e.m.f. variation was observed in a test solution, it was always of type C_1. On the other hand, with one exception, all the D_1 and D_2 transients in the test solutions were shown by electrodes Nos. 5 and 6, and these rarely gave response of type C_1. (One example of type D_2 response with a test solution was shown by electrode No. 14). C_1 response after transfer to standard solution 2 was only observed for electrodes Nos. 1 and 8 and in each case was preceded by C_1 response in the test solution.

The type of C_1 response observed in these experiments might be termed

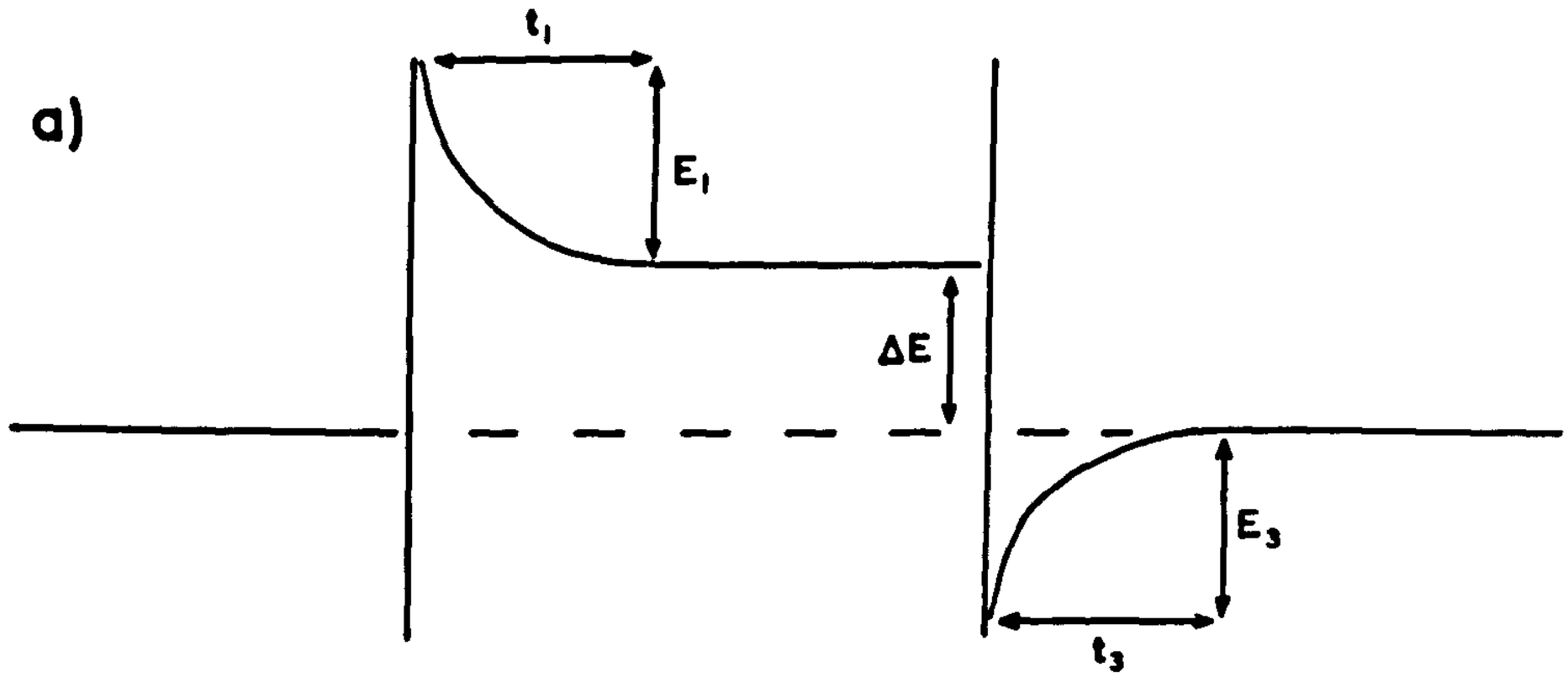


Fig. 26 The Response of Soda Glass Electrodes in Alkaline Solutions.

TABLE 8.3. Transients shown by E.I.L. GG 33 Electrodes.

Experiments with 1.0m Sodium Solutions.

ΔE, E_1, E_2, E_3 and E_4 in mV. t_1, t_2, t_3 and t_4 in minutes.

Electrode No. 1.

p_wH	Date	Test	ΔE	E_1 t_1	E_2 t_2	E_3 t_3	E_4 t_4
8.83	17/5/65	84	+2.1	E		0.8 3	D_1
	17/5/65	85	+2.2	C_1	0.3 6	1.1 3	D_1
9.85	4/8/65	132	+8.0	C_1	1.0 10	E	
10.49	29/7/65	123	+15.2	C_1	2.0 26	C_1	0.3 13
	4/8/65	133	+16.4	C_1	1.6 15	C_1	0.4 6

Electrode No. 5

p_wH	Date	Test	ΔE	E_1 t_1	E_2 t_2	E_3 t_3	E_4 t_4
8.83	11/5/65	79	+1.3	0.8 1	0.3 10	1.0* 6	D_1
9.84	21/12/65	185	+6.3	1.2 2	0.4 11	2.1 5	D_1
9.85	29/7/65	127	+6.2	0.3 1	D_1	1.5 4	D_1
	4/8/65	135	+8.0	C_1	0.4 9	0.5 1	D_1
	11/8/65	146	+6.8	1.5 1	0.7 14	0.7 2	D_1
10.49	29/7/65	128	+15.0	0.7 2	0.4 11	1.7 4	D_1
	4/8/65	134	+17.5	C_1	1.0 10	0.9 2	0.4 11
	11/8/65	147	+15.8	0.9 1	0.6 10	0.9 2	D_1
	11/8/65	149	+15.9	1.2 1	0.8* 10	0.4* 2	0.3 8
10.55	6/5/66	215	+17.7	4.2 2	0.5 18	5.8 5	D_1
	6/5/66	216	+17.9	14 5	D_1*	7.3* 8	D_1

TABLE 8.3 (Cont)

Electrode No. 6.

p_wH	Date	Test	ΔE	E_1	t_1	E_2	t_2	E_3	t_3	E_4	t_4
8.83	19/5/65	90	+1.7	0.7	1	0.6	13	0.5	6	D_1	
	19/5/65	91	+1.8	0.4	1	0.5	10	0.3	2	D_1	
	21/5/65	94	+2.2	C_1		0.4*	5	1.8*	6	D_1	
	21/5/65	95	+2.2	0.4	1	0.3*	9	1.6*	8	D_1	
	21/5/65	96	+2.3	0.3	1	0.3*	8	0.8	5	D_1	
	21/5/65	97	+2.2	E				1.0	5	D_1	
9.85	11/8/65	140	+6.1	0.4	1	0.5	10	0.8	4	D_1	
10.49	11/8/65	142	+15.4	0.8	2	2.5	60	1.0	5	D_1	

Electrode No. 8.

p_wH	Date	Test	ΔE	E_1	t_1	E_2	t_2	E_3	t_3	E_4	t_4
8.83	11/5/65	75	+1.1	C_1		0.3	5	E			
	17/5/65	82	+1.5	C_1		0.8	18	0.7	2	D_1	
	17/5/65	83	+1.4	C_1		0.4	8	E			
9.16	3/8/66	218	+2.0	E^x				0.5^x	1	D_1	
9.85	10/8/65	136	+5.4	C_1		0.9	12	E			
	10/8/65	139	+5.4	C_1		0.7*	13	E*			
10.49	10/8/65	137	+13.0	C_1		1.7	19	C_1		0.6	10
10.55	5/5/66	213	+16.0	C_1		3.7	90	C_1		0.7	10

x Acetate Buffer as standard solution.

TABLE 8.3 (Cont.)

Electrode No. 12.

p_wH	Date	Test	ΔE	E_1 t_1	E_2 t_2	E_3 t_3	E_4 t_4
9.14	10/8/66	225	+3.1	E		1.2 3	D_1
	10/8/66	228	+3.3	C_1	0.6* 1	0.8* 5	D_1
9.16	10/8/66	226	+3.1	E		0.9 3	D_1
	10/8/66	227	+3.2	E		1.4 3	D_1
9.84	21/12/65	179	+8.0	C_1	1.0 18	E	
10.04	4/11/65	156	+9.3	C_1	1.3* 18	0.8* 3	D_1
	12/11/65	161	+10.1	C_1	1.3* 14	0.7* 2	D_1
13.00	4/11/65	157	+107	C_1	5.1* 60	2.1* 40	D_1

Electrode No. 14

p_wH	Date	Test	ΔE	E_1 t_1	E_2 t_2	E_3 t_3	E_4 t_4
8.83	11/5/65	353	+1.0	0.5 1	0.2 8	0.8 8	D_1
	19/5/65	355	+1.2	C_1	0.7 7	0.4 4	D_1
	21/5/65	357	+1.1	E		0.7* 10	D_1

"C_1 Drift" since both $\left|\frac{dE}{dt}\right|$ and $\left|\frac{d^2E}{dt^2}\right|$ were small, thus making it possible to extrapolate the curves back to the instant of transfer. Hence the question arose as to which was the most appropriate value of the final error in the test solution. It could either be computed in the usual manner relative to the average of the steady e.m.f's observed for the standard solution before and after transfer to the test solution, or obtained from the e.m.f. difference at the instant of transfer back to the standard solution. The former procedure was adopted since not only was it more consistent with the treatment of the other types of response observed but also the instantaneous errors did not appear to have any particular significance. For example, the instantaneous errors ΔE_A and ΔE_B in figure 26c, for the transfer of an electrode from a standard solution to the test solution and from the test solution back to a standard solution were not the same, and the instantaneous errors shown by different electrodes giving this response showed no better agreement than the errors determined by the other method.

It was mentioned in section 5.4. that in some cases a change of asymmetry potential was observed during a test of a glass electrode and this was allowed for when calculating the glass electrode error. It was pointed out that such a change sometimes appeared to be a result of immersing the glass electrode in the test solution in question and an example of this was shown by electrode No. 8 in test 213 (5/5/66). In this experiment the electrode showed C_1 response in the sodium solution p_wH 10.55 and after it had been in the solution for 15 minutes showed an error of 15.6mV. The error was still changing and increased

by 0.1mV during the next 4 minutes. The e.m.f. was not observed again until about an hour later and it was then found that the error had risen to 17.2mV but was apparently now constant. However when the electrode was transferred back to a standard solution, the steady e.m.f. observed after the initial small transient had died away, showed that the asymmetry potential had changed, resulting in an increase in the calibration e.m.f. of 1.2mV. The final error for the test solution relative to this new value of the calibration e.m.f. was 16.0mV, only slightly different to that observed earlier. Hence this value has been recorded in the various tables. A further example of this type of result was test 142 for electrode No. 6 (11/8/65) for which the error given in the tables, was obtained in a similar manner.

The errors shown by the two Jena H electrodes when tested in 1.0m sodium solutions are given in table 8.4 and are also illustrated in figure 25 together with the results for the GG 33 electrodes. Again it is seen that the electrodes differed slightly, one giving consistently larger errors than the other, but excellent reproducibility was obtained on repeated testing of an electrode in a particular solution during a single experimental run. The transients observed for the Jena H electrodes during these experiments are given in table 8.5. They were much smaller than those shown by the GG 33 electrodes and in some cases no transient was observed at all (type E response). It was therefore difficult to make generalisations but it appeared that these electrodes were showing similar behaviour to the GG 33 electrodes, only on a smaller scale. For example, electrode No. 21 tended to give a small D_1

TABLE 8.4. Alkaline Errors of Jena H Electrodes

1.0m Sodium Solutions

p_wH	Electrode No. 9			Electrode No. 21		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.04	22/4/66	207	+1.3	22/4/66	211	+1.0
9.14				9/8/66	221	+1.3
9.16				9/8/66	222	+1.4
9.84	22/12/65	189	+4.4	4/1/66	193	+3.6
	22/12/65	190	+4.5	4/1/66	194	+3.6
10.04	12/11/65	239	+5.1	12/11/65	164	+4.1
				12/11/65	165	+4.2
10.55	22/4/66	208	+11.0	22/4/66	212	+10.0

1.0m Lithium Solution

p_wH	Electrode No. 9			Electrode No. 21		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
10.74	22/12/65	188	+3.1	17/12/65	176	+2.5

TABLE 8.5. Transients shown by Jena H Electrodes

Experiments with 1.0m Sodium Solutions.

ΔE, E_1, E_2, E_3 and E_4 in mV. t_1, t_2, t_3 and t_4 in minutes

Electrode No. 9.

p_wH	Date	Test	ΔE	E_1	t_1	E_2	t_2	E_3	t_3	E_4	t_4
9.04	22/4/66	207	+1.3	C_1		3±1	3	2.3	2	D_1	
9.84	22/12/65	189	+4.4	C_1		0.4	10			E^*	
	22/12/65	190	+4.5	C_1^*		0.3	7	0.4	8	D_1	
10.04	12/11/65	239	+5.1	E				0.6	5	D_1	
10.55	22/4/66	208	+11.0	C_1		0.7	16	1.9	5	D_1	

Electrode No. 21

p_wH	Date	Test	ΔE	E_1	t_1	E_2	t_2	E_3	t_3	E_4	t_4
9.04	22/4/66	211	+1.0	E						E	
9.14	9/8/66	221	+1.3	E						E	
	9/8/66	222	+1.4	E						E	
9.84	4/1/66	193	+3.6	1.0	1	D_1				E	
	4/1/66	194	+3.6	0.3	1	D_1^*				E^*	
10.04	12/11/65	164	+4.1	C_1		0.3	10	0.7	5	D_1	
	12/11/65	165	+4.2	E^*				0.4	2	D_1^*	
10.55	22/4/66	212	+10.0	C_1		0.6	20	-		-	

* Indicates a transfer from or to an acid standard solution.

transient in the test solution whereas electrode No. 9 usually showed a slight C_1 drift.

Tables 8.3 and 8.5 contain data which show that the response of a glass electrode was independent of the buffer used to fix the pH of the solution. The solution of p_wH 9.14 was a tris buffer with added sodium chloride whereas that of p_wH 9.16 contained borax and sodium chloride. Electrode No. 12 (GG 33) and electrode No. 21 (Jena H) were each tested in both these solutions during a single experimental run and it can be seen that for each electrode, the response and the magnitude of the final error were independent of the background buffer.

The errors shown by the GG 33 electrodes in 1.0m lithium and potassium solutions are given in tables 8.6 and 8.7. Again the errors were very reproducible for a particular electrode over a fairly short period. However comparison of the data for electrodes Nos. 5, 8 and 12 in potassium solutions of about the same p_wH (10.01 and 10.09 in 1965 and 10.05 in 1966) indicates that the errors increase as the electrodes become older. The relative magnitudes of the sodium, lithium and potassium errors shown by one particular GG 33 electrode at about the same time are shown in figure 27. The Jena H electrodes were only tested in one lithium solution and the observed final errors are given in table 8.4. It may be seen that these errors were smaller than those observed for the same electrodes in sodium solutions.

When tested in 1 molal lithium solutions the GG 33 electrodes gave more D transients than in sodium solutions, that is the initial decrease in error

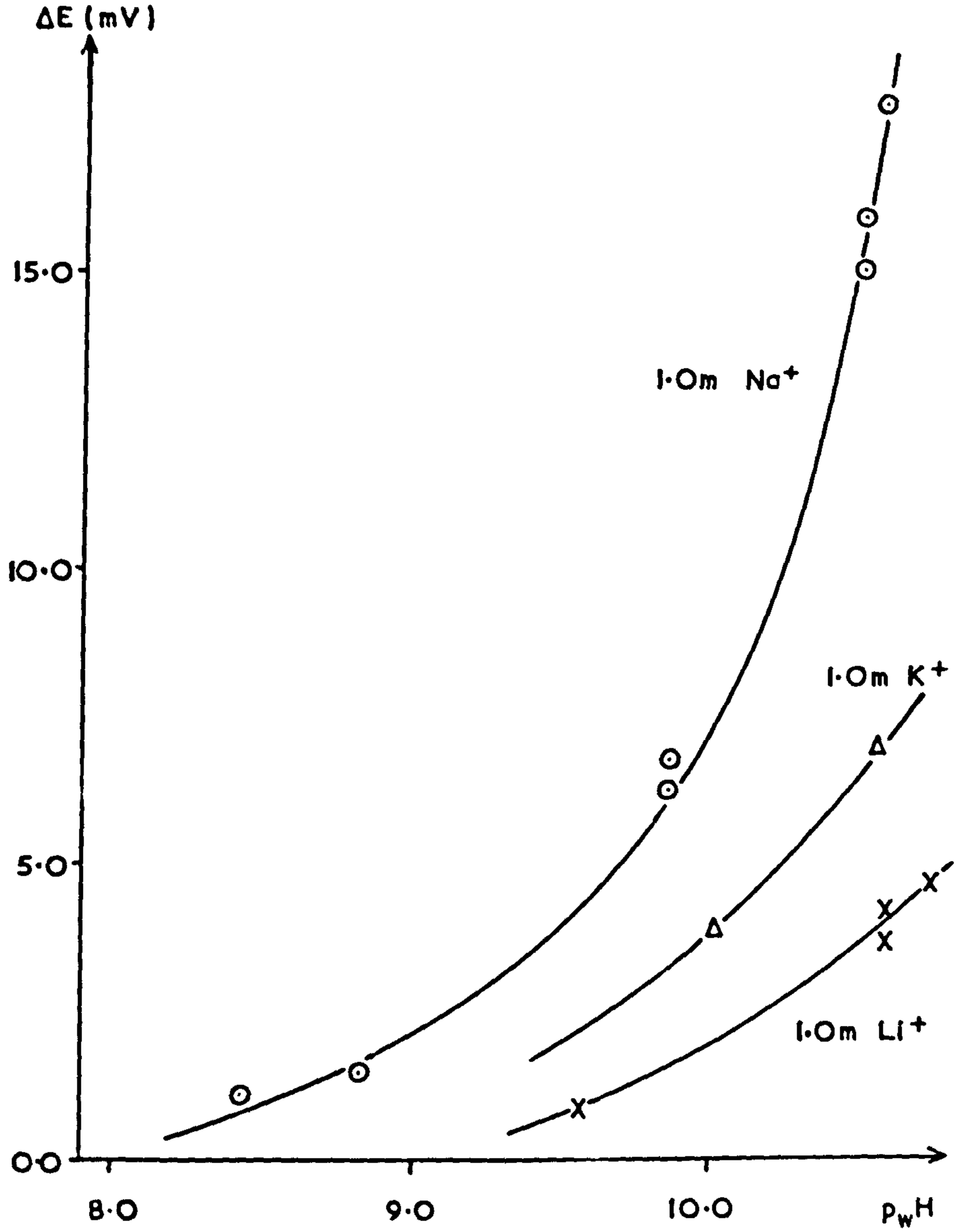


Fig. 27 THE ALKALINE ERRORS OF E.I.L. GG 33 ELECTRODE No. 5

TABLE 8.6. Errors of E.I.L. GG 33 Electrodes in 1.0m Lithium Solutions

p_wH	Electrode No. 1.			Electrode No. 5.		
	Date	Error (mV.)	Test	Date	Error (mV.)	Test
9.56				24/8/65	+0.8	150
10.59				11/8/65	+4.2	148
				24/8/65	+3.7	151
10.74	10/12/65	+4.1	169	21/12/65	+4.7	184
	17/12/65	+4.3	173			

p_wH	Electrode No. 6.			Electrode No. 8.			Electrode No. 12.		
	Date	Error (mV.)	Test	Date	Error (mV.)	Test	Date	Error (mV.)	Test
8.48				24/7/64	+0.3	331			
9.27				24/7/64	+0.6	332			
10.59	11/8/65	+3.6	141	10/8/65	+2.9	138			
10.74							21/12/65	+5.7	180

TABLE 8.7.

Errors of E.I.L. GG 33 Electrodes in 1.0m Potassium Solutions

p_wH	Electrode No. 1			Electrode No. 5		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.04	10/12/65	168	+0.9			
	17/12/65	172	+1.2			
9.13				17/8/66	234	+2.2
10.01	13/7/65	116	+3.1	13/7/65	121	+3.9
				13/7/65	122	+3.9
10.05				17/8/66	233	+5.9
				17/8/66	235	+5.8
10.09	1/6/65	362	+2.8			
10.54	13/7/65	117	+4.5			
	13/7/65	119	+4.4			
10.56				18/6/65	108	+7.0

TABLE 8.7. (Cont.)

p_wH	Electrode No. 8			Electrode No. 12			Electrode No. 14		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)	Date	Test	Error (mV.)
9.13	17/8/66	229	+0.8						
10.01	14/6/65	106	+2.4	13/7/65	112	+3.2	14/6/65	363	+1.1
	14/6/65	107	+2.6	13/7/65	114	+3.0			
10.01*	14/6/65	101	+2.2				14/6/65	365	+1.1
10.09	14/6/65	102	+2.2						
10.09	1/6/65	359	+2.3						
	14/6/65	105	+2.3						
10.05	17/8/66	230	+3.0	17/8/66	236	+4.7			
10.54				13/7/65	113	+5.2			
				13/7/65	115	+5.2			
10.56	14/6/65	103×	+3.8				14/6/65	364	+1.7
	14/6/65	104	+3.8						
	18/6/65	110	+4.1						

* During these experiments the electrodes were transferred directly between the solutions of p_wH 10.01 (0.1m Br^-/E + 1.0m KBr) and p_wH 10.09 (0.1m Cl^-/E + 1.0m KCl)

× In this test the electrode was transferred from and to the 0.1m Cl^-/Ethanolamine buffer + 1.0m KCl of p_wH 10.56.

was generally more prominent, and for potassium solutions they invariably showed type D_1 response, both after transfer to the potassium solution itself and after transfer back to a standard solution, i.e. exactly as shown in figure 26a. The transients are presented in tables 8.8 and 8.9, and table 8.10 gives details of the transients observed during experiments involving 2.0m potassium solutions. The 1.0m potassium solution of p_wH 10.01 contained only bromide as the anion whereas chloride was the only anion in the other potassium solutions. The type of response shown by the electrodes was apparently uninfluenced by the anion in the test solution, and the data obtained with electrodes Nos. 8 and 14, for solutions of the same cation content, almost the same p_wH (10.01 and 10.09) but different anions, show that the magnitude of the error was also independent of the anion. No transients were observed when the electrodes were transferred directly between these two solutions.

A further example of an experiment in which a change of asymmetry potential occurred while the glass electrode was placed in the test solution, is that for electrode No. 12 with 1m potassium solution p_wH 10.54 on 13/7/65 (Test 115). The error shown by the electrode in this solution after the usual D_1 transient had died away, was 5.2mV and was constant for 4 minutes. The electrode was then left in the solution for about 2 hours and at the end of this time the e.m.f., which was observed to be constant for 7 minutes, showed an error of 5.9mV relative to standard solution 1. On transferring the electrode back to the standard solution the final steady value of the

TABLE 8.8. Transients shown by E.I.L. GG 33 Electrodes - Experiments with 1.0m Lithium Solutions.

ΔE, E_1, E_2, E_3 and E_4 in mV. t_1, t_2, t_3 and t_4 in minutes

	p_wH	Date	Test	ΔE	E_1	t_1	E_2	t_2	E_3	t_3	E_4	t_4
Electrode No. 1	10.74	10/12/65	169	+4.1	0.3	1	0.3	10	1.3	4	D_1	
		17/12/65	173	+4.3	2.2*	8	D_1		2.3*	10	D_1	
Electrode No. 5	9.56	24/8/65	150	+0.8	0.5	5	D_1		0.3	2	D_1	
	10.59	11/8/65	148	+4.2	0.4	2	D_1		1.8	3	D_1	
		24/8/65	151	+3.7	0.5	4	D_1		1.9	4	D_1	
	10.74	21/12/65	184	+4.7	1.5	6	D_1		3.2	10	D_1	
Electrode No. 6	10.59	11/8/65	141	+3.6	1.0	3	0.4	14	1.8	7	D_1	
Electrode No. 8	8.48	24/7/64	331	+0.3	C_1		0.3	2	0.3	3	D_1	
	9.27	24/7/64	332	+0.6	E				0.4	3	D_1	
	10.59	10/8/65	138	+2.9	C_1		0.3	10	0.5	1½	0.3	6
Electrode No. 12	10.74	21/12/65	180	+5.7	C_1		0.6	13	0.6	2	D_1	

TABLE 8.9 Transients shown by E.I.L. GG 33 Electrodes

Experiments with 1.0m Potassium Solutions.

ΔE, E_1 and E_3 all in mV. t_1 and t_3 in minutes.

All transients of type D_1.

Electrode No. 1

p_wH	Date	Test	ΔE	E_1	t_1	E_3	t_3
9.04	10/12/65	168	+0.9	E		0.5	2
	17/12/65	172	+1.2	E		0.7	3
10.01	13/7/65	116	+3.1	0.7*	3	0.7*	2
10.09	1/6/65	362	+2.8	0.7	1	0.8	3
10.54	13/7/65	117	+4.5	1.1*	4	0.8*	3
		119	+4.4	1.5*	6	-	-

Electrode No. 5

p_wH	Date	Test	ΔE	E_1	t_1	E_3	t_3
9.13	17/8/66	234	+2.2	1.3	4	2.8	8
10.01	13/7/65	121	+3.9	1.9*	7	1.1*	7
	13/7/65	122	+3.9	2.6	7	-	-
10.05	17/8/66	233	+5.9	3.2	15	2.1	9
	17/8/66	235	+5.8	3.3*	15	2.1*	10
10.56	18/6/65	108	+7.0	2.9	10	2.2	6

TABLE 8.9. (Cont)

Electrode No. 8.

p_wH	Date	Test	ΔE	E_1	t_1	E_3	t_3
9.13	17/8/66	229	+0.8	E^x		E^x	
10.01	14/6/65	106	+2.4	1.5	6	0.9	4
	14/6/65	107	+2.6	2.7*	8	1.1*	5
10.01 }	14/6/65	101	+2.2	E		0.6	3
10.09 }	14/6/65	102	+2.2	1.0	3	0.3*	2
10.09	14/6/65	105	+2.3	1.4*	4	0.4*	2
	1/6/65	359	+2.3	E		1.0	2
10.05	17/8/66	230	+3.0	0.8	2	0.6	2
10.56	14/6/65	104	+3.8	2.1*	6	0.5*	4
	18/6/65	110	+4.1	1.0	2	0.7	2

Electrode No. 12.

p_wH	Date	Test	ΔE	E_1	t_1	E_3	t_3
10.01	13/7/65	112	+3.2	0.6	1	0.6	2
	13/7/65	114	+3.0	1.4*	3	1.0*	2
10.05	17/8/65	236	+4.7	2.5^x	6	1.5^x	4
10.54	13/7/65	113	+5.2	1.4	3	0.8*	3
		115	+5.2	1.6*	5	0.4*	2

^{x} Acetate Buffer as standard solution.

TABLE 8.9 (Cont)

Electrode No. 14

p_wH	Date	Test	Error	E_1	t_1	E_3	t_3
10.01	14/6/65	363	+1.1	E		0.4	6
10.01 } 10.09 }	14/6/65	365	+1.1	E*		0.3*	5
10.56	14/6/65	364	+1.7	0.3*	2	0.3*	4

TABLE 8.10

Transients shown by E.I.L. GG 33 Electrodes

Experiments with 2.0m Potassium Solution p_wH 10.65

ΔE, E_1 and E_3 in mV. t_1 and t_3 in minutes.

All transients of type D_1.

	Date	Test	ΔE	E_1	t_1	E_3	t_3
Electrode No. 1.	13/7/65	118	+6.6	2.5*	8	1.3*	5
Electrode No. 5.	18/6/65	109	+9.9	5.3	11	3.0	5
	13/7/65	120	+10.0	5.7*	15	1.5	5
Electrode No. 8.	18/6/65	111	+5.3	1.3	6	0.9	3

calibration e.m.f. was found to be 0.8mV higher than that observed at the beginning of the experiment. The final error relative to this new value was only 5.1mV and hence the increase in e.m.f. observed while the glass electrode was placed in the potassium solution, could be accounted for as a change of asymmetry potential. The error therefore might be regarded as having been constant at about 5.2mV, the value recorded in the tables. A similar result was obtained for electrode No. 1 in test 172 (17/12/65). This experiment also involved a potassium solution and again the electrode was left in the solution for an exceptionally long time.

In tables 8.3, 8.8, 8.9 and 8.10 as in the tables of transients in the last chapter, where a transient is marked with an asterisk the electrode was transferred either from or to an acid standard solution. Several pairs of experiments are to be found in these tables where a given electrode was tested twice in an alkaline solution, first relative to an acid standard solution such as 0.1m H_2SO_4, and then relative to a tris or ethanolamine buffer as standard solution. The results of these experiments indicate that the response and the magnitude of the error were independent of the pH of the standard solution.

CHAPTER 9.

The Effect of Acids upon pH Responsive Glass Electrodes

Although the present investigation was mainly concerned with the response of glass electrodes in the alkaline pH range, some experiments were also carried out with acid solutions in order to compare, where possible, the response associated with the negative acid errors with that observed in the alkaline region for the same electrodes. However, as was noted in chapter 6, the lithia glass electrodes showed no errors in the acid solutions and therefore most of what follows is concerned with the soda glass electrodes. Nevertheless the lithia glass electrodes did show negative errors in a fluoride solution of pH 4.8 and these results will be discussed later in this chapter.

The soda glass electrodes were tested in various HCl solutions and, as was expected from the work of Caudle[1], they showed negative errors which increased with increasing HCl molality. The electrodes were also tested in two HCl - NaCl mixtures. For the first of these, 0.01m HCl + 1.0m NaCl, no errors were observed, but for the second 0.1m HCl + 1.0m NaCl they gave the errors shown in table 9.1. From these experiments it was found that the magnitudes of the errors were also dependent upon the total chloride ion molality at constant acid concentration, and upon the acid concentration at constant chloride ion molality.

It can be seen from table 9.1 that the errors in the acid solutions were less reproducible than the alkaline errors of these electrodes. There was a

TABLE 9.1.

Errors of Soda Glass Electrodes in HCl Solutions.

Solution	Electrode No. 1 (GG 33)			Electrode No. 5 (GG 33)		
	Date	Test	Error (mV)	Date	Test	Error (mV)
0,1m HCl	9/7/64	286	-0.4	9/7/64	295	-0.4
	10/7/64	313	-0.4	9/7/64	299	-0.4
	10/7/64	315	-0.4	18/8/64	333	-0.4
	17/5/65	86	-0.5	18/8/64	334	-0.4
				5/11/64	340	-0.5
				5/11/64	341	-0.6
0.1m HCl	9/7/64	284	-1.4	9/7/64	296	-2.3
+1.0m NaCl*	10/7/64	312	-1.4	9/7/64	297	-2.4
				9/7/64	300	-2.5
0.5m HCl	17/5/65	87	-3.7	5/11/64	342	-6.3
	17/5/65	88	-3.7	11/5/65	80	-9.5
	29/7/65	124	-6.0	29/7/65	129	-14.2
	10/12/65	170	-6.3	24/8/65	152	-12.8
1.0m HCl	29/7/65	125	-12.8	29/7/65	130	-28.1
	14/4/66	201	-15.2	19/4/66	206	-33.5
	14/4/66	202	-15.6			

* Electrodes Nos. 1 and 5 were tested in 0.1m HCl + 1.0m NaCl using 0.1m HCl as the standard solution. These electrodes were showing small errors in the 0.1m HCl at this time and the errors in this table have therefore been corrected to allow for the errors in the 0.1m HCl

TABLE 9.1. (Cont.)

Solution	Electrode No. 8 (GG 33)			Electrode No. 12 (GG 33)		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)
0.1m HCl	1/6/65	360	-0.3			
	14/4/66	205	-0.5			
0.1m HCl	9/7/64	293	-0.5	21/7/64	321	-0.7
+1.0m NaCl	21/7/64	317	-0.7			
	21/7/64	318	-0.6			
0.5m HCl	5/11/64	335	-1.5	9/11/64	343	-3.0
	5/11/64	338	-1.6	12/11/65	162	-10.1
	11/5/65	76	-2.9	17/8/66	237	-12.8
	11/5/65	77	-2.8			
	17/8/66	231	-8.0			
1.0m HCl	14/4/66	203	-14.1	4/11/65	158	-28.2

Solution	Electrode No. 6 (GG 33)			Electrode No. 14 (GG 33)			Electrode No. 21 (Jena H)		
	Date	Test	Error (mV.)	Date	Test	Error (mV.)	Date	Test	Error (mV.)
0.1m HCl	18/6/64	280	-0.3						
0.5m HCl	19/5/65	92	-6.2	11/5/65	354	-0.3	12/11/65	166	-0.9
	21/5/65	98	-6.8	19/5/65	356	-0.2			
				21/5/65	358	-0.4			
1.0m HCl	11/8/65	143	-26.1	14/4/66	366	-1.4	4/1/66	195	-3.6
							4/1/66	197	-4.0
							4/1/66	199	-4.0

large variation in the magnitudes of the errors shown by different electrodes in the same solution and for a given electrode the error in a particular HCl solution usually increased considerably as the electrode became older. Nevertheless the electrode age was apparently not the only factor which determined the magnitude of the error shown in a given solution, since although the electrode ages increase with decreasing numerical order, at any given time, electrode No. 1 showed smaller errors than electrodes Nos. 5 and 6. Similarly electrode No. 8 showed smaller errors than electrode No. 12. Despite the poor reproducibility shown by these errors as a whole, good agreement was sometimes obtained between the values observed on repeated testing of an electrode during the same experimental run.

The main features of the transients shown by the soda glass electrodes when tested in HCl solutions are given in table 9.2. The electrodes frequently gave type D_1 response both after transfer to an HCl solution and after transfer back to a standard solution. However it would appear that if an electrode had been standing for a few months in distilled water, without being tested in alkaline solutions, type C response might be observed. For example, in May 1965 after such a period, all the electrodes tested in 0.5m HCl (Nos. 1, 5, 6 and 8) gave response of type C in the HCl solution followed by type D_1 response on being transferred back to a standard solution. During the succeeding two months, the electrodes Nos. 1 and 5 were tested in alkaline solutions while electrode No. 6 was kept in distilled water. When they were again tested in HCl solutions, it was found that the response of electrodes

TABLE 9.2

Transients shown by Soda Glass Electrodes during Experiments with HCl Solutions.

Section (a) All transients in Standard Solution 2 type D_1 unless otherwise stated. Details of other transients given in section (b)

Electrode No. 1

Solution	Date	Test	ΔE	Test Solution					Standard Solution	
			mV		mV	min	mV	min	mV	min
0.1m HCl	9/7/64	286	-0.4	D_1	1.3	4			0.3	1
	17/5/64	86	-0.5	D_1	0.6	2			C_1	
0.1m HCl*	9/7/64	284	-1.0	D_1	1.6	3			2.1	5
+1.0m NaCl	10/7/64	312	-1.0	D_1	1.8	5			1.7	5
0.5m HCl	17/5/65	87	-3.7	C_1	0.5	2			2.4	8
	17/5/65	88	-3.7	C_2	1.1	2	0.6	8	2.3	10
	29/7/65	124	-6.0	D_2	3.3	4	0.4	15	1.8	4
	10/12/65	170	-6.3	C_2	1.3	½	5.7	15	2.7	13
1.0m HCl	29/7/65	125	-12.8	D_1	8.6	15			2.9	6
	14/4/66	201	-15.2	C_2	9.3	2	1.3	13	6.9	10
	14/4/66	202	-15.6	C_2	4.5	1	3.7	14	10.0	10

TABLE 9.2 (Cont)

Electrode No. 5.

Solution	Date	Test	ΔE		Test Solution				Standard Solution	
			mV		mV	min	mV	min	mV	min
0.1m HCl	9/7/64	295	-0.4	D_1	2.2	4			0.5	1
	9/7/64	299	-0.4	D_1	2.0	2			0.5	1
	18/8/64	333	-0.4	D_1	1.3	6			D_2	
	18/8/64	334	-0.4	D_1	2.3	5			1.1	5
	5/11/64	340	-0.5	D_1	0.6	10			E	
	5/11/64	341	-0.6	D_1	0.6	6			0.6	4
0.1m HCl*	9/7/64	296	-1.9	D_1	1.4	5			2.6	7
+1.0m NaCl	9/7/64	297	-2.0	D_1	2.8	7			2.6	7
	9/7/64	300	-2.1	D_1	1.3	4			2.6	8
	10/7/64	310	-2.4	D_1	1.9	2			1.4	2
0.5m HCl	5/11/64	342	-6.3	C_2	0.8	½	2.5	10	1.2	8
	11/5/65	80	-9.5	C_1	7.4	15			2.9	6
	29/7/65	129	-14.2	D_1	9.0	21			4.6	6
	24/8/65	152	-12.8	D_1	12.8	35			5.0	15
1.0m HCl	29/7/65	130	-28.1	D_1	16.6	32			9.9	15
	19/4/66	206	-33.5	C_2'	26.8	7	1.6	43	13.2	10

* Electrodes Nos. 1 and 5 were tested in 0.1m HCl + 1.0m NaCl using 0.1m HCl as the standard solution. These electrodes were showing small errors in 0.1m HCl at this time but in this table the errors are the values observed relative to the 0.1m HCl

TABLE 9.2 (Cont)

Electrode No. 6

Solution	Date	Test	ΔE	Test Solution					Standard Solution	
			mV		mV	min	mV	min	mV	min
0.1m HCl	18/6/64	280	-0.3	D_1	1.2	5			0.7	2
0.5m HCl	19/5/65	92	-6.2	C_1	4.2	8			3.4	8
	21/5/65	98	-6.8	C_2	4.1	3	0.7	17	5.0	8
1.0m HCl	11/8/65	143	-26.1	C_2	9.7	1	3.0	7	D_2	

Electrode No. 8

Solution	Date	Test	ΔE	Test Solution					Standard Solution	
			mV		mV	min	mV	min	mV	min
0.1m HCl	5/11/64	336	-0.1	D_1	0.5	4			E	
	5/11/64	337	-0.1	D_1	0.5	3			E	
	1/6/65	360	-0.3	D_1	2.3	5			E	
	14/4/66	205	-0.5	D_1	5.3	9			-	
0.1m HCl	9/7/64	293	-0.5	D_1	1.0	5			0.6	2
+1.0m NaCl	21/7/64	317	-0.7	D_1	0.6	3			0.7	1
	21/7/64	318	-0.6	D_1	0.8	2			0.8	3
0.5m HCl	5/11/64	335	-1.5	D_1	2.8	10			1.7	2
	5/11/64	338	-1.6	D_1	2.5	5			1.8	5
	11/5/65	76	-2.9	C_2	1.0	1	1.3	8	2.3	6
	11/5/65	77	-2.8	C_2	0.4	½	2.2	10	-	
	17/8/66	231	-8.0	D_1	6.2	10			3.4	4
1.0m HCl	14/4/66	203	-14.1	C_2	5.9	½	4.3	15	7.5	8

TABLE 9.2 (cont)

Electrode No. 12

Solution	Date	Test	ΔE		Test Solution				Standard Solution	
			mV		mV	min	mV	min	mV	min
0.1m HCl	9/11/64	344	-0.3	D_1	1.4	6			0.6	1
	9/11/64	345	-0.2	D_1	1.2	10				E
0.1m HCl +1.0m NaCl	21/7/64	321	-0.7	E					1.5	2
0.5m HCl	9/11/64	343	-3.0	D_1	7.0	12			2.7	4
	12/11/65	162	-10.1	D_1	4.3	3				D_2
	17/8/66	237	-12.8	C_1	6.9	5			2.9	5
1.0m HCl	4/11/65	158	-28.2	D_2	11($\pm$1)	2	3.5	28	3.6	48

Electrode No. 14.

Solution	Date	Test	ΔE		Test Solution				Standard Solution	
			mV		mV	min	mV	min	mV	min
0.5m HCl	11/5/65	354	-0.3	D_1	0.4	5				D_2
	19/5/65	356	-0.2	D_1	0.4	4				-
	21/5/65	358	-0.4	E						E
1.0m HCl	14/4/66	366	-1.4	E					0.9	2

TABLE 9.2 (Cont)

Electrode No. 21

Solution	Date	Test	ΔE	Test Solution					Standard Solution	
			mV		mV	min	mV	min	mV	min
0.5m HCl	12/11/65	166	-0.9	D_1	0.5	2			E	
1.0m HCl	4/1/66	195	-3.6	D_1	0.6	2			0.6	1
	4/1/66	197	-4.0	D_2	1.0	2	0.3	13	0.4	2
	4/1/66	199	-4.0	D_1	1.2	3			0.7	2

Section (b)

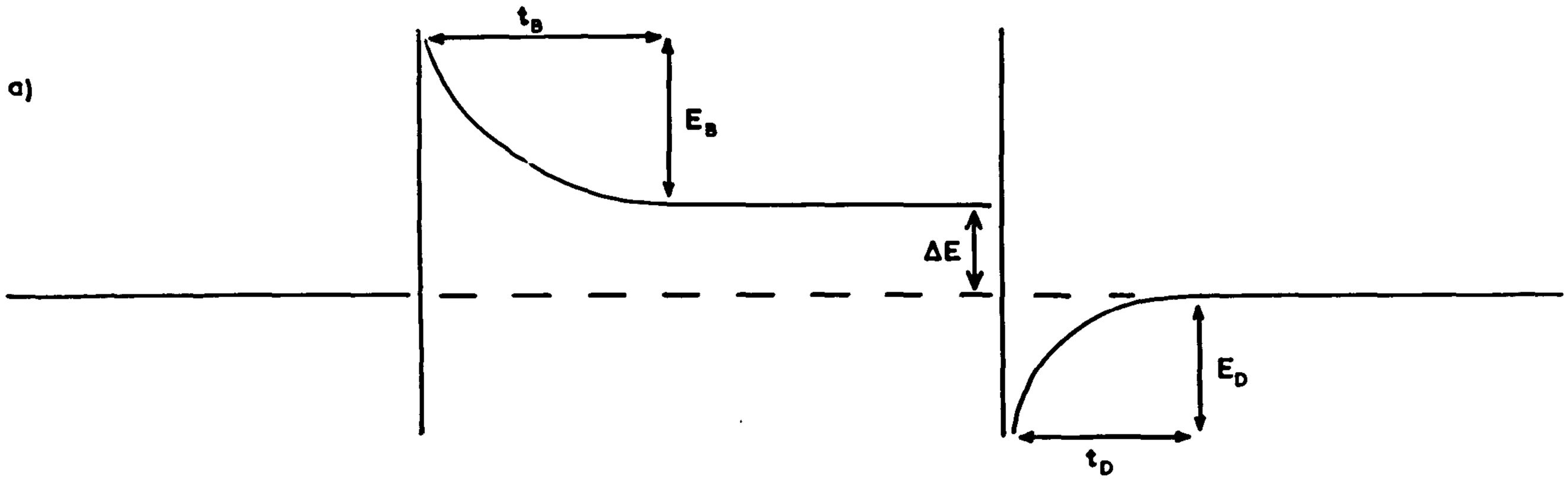
Electrode	Solution	Test	ΔE	Test Solution	Standard Solution 2				
			mV	Response	Response	mV	min	mV	min
No. 1	0.1m HCl	86	-0.5	D_1	C_1	0.5	2		
No. 5	0.1m HCl	333	-0.4	D_1	D_2	0.6	½	0.3	8
No.6	1.0m HCl	143	-26.1	C_2	D_2	4.4	3	1.4	33
No. 12	0.5m HCl	162	-10.1	D_1	D_2	1.7	2	0.3	11
No. 14	0.5m HCl	354	-0.3	D_1	D_2	0.3	1	0.3	5

Nos. 1 and 5 in the acid solutions, had reverted to type D (in most cases type D_1), whereas the response of electrode No. 6 was again of type C (Tests 124, 125, 129, 130, 143 and 152). A similar change in response was also recorded for electrodes Nos. 1, 5 and 8 in April 1966.

It was also observed that the testing of a soda glass electrode in an HCl solution in which it gave a negative error, produced a marked change in the manner in which it responded in alkaline solutions containing sodium, potassium or lithium ions. A typical experimental run for the investigation of this effect included the following solutions:

1. Buffer Solution pH 8 - 10.5 with 1.0m Na^+, K^+ or Li^+
2. Buffer Solution pH 8 - 10.5
3. 0.1m H_2SO_4
4. HCl (1.0m or 0.5m).

An electrode was first tested in the molal sodium, potassium or lithium solution relative to the buffer as standard solution and then was tested in the hydrochloric acid using the 0.1m H_2SO_4 as standard. Next it was transferred from the sulphuric acid back to the alkaline standard solution, and within the precision of the experimental method no error was observed, thus showing that its pH response had not been impaired. However when the electrode was again tested in the buffer solution containing alkali metal ions the positive error was found to be significantly larger than it had been immediately before testing in the HCl. Furthermore large transients, usually of type D_1 (figure 28a), were now observed irrespective of which type of response had been observed previously. The Jena H electrodes invariably



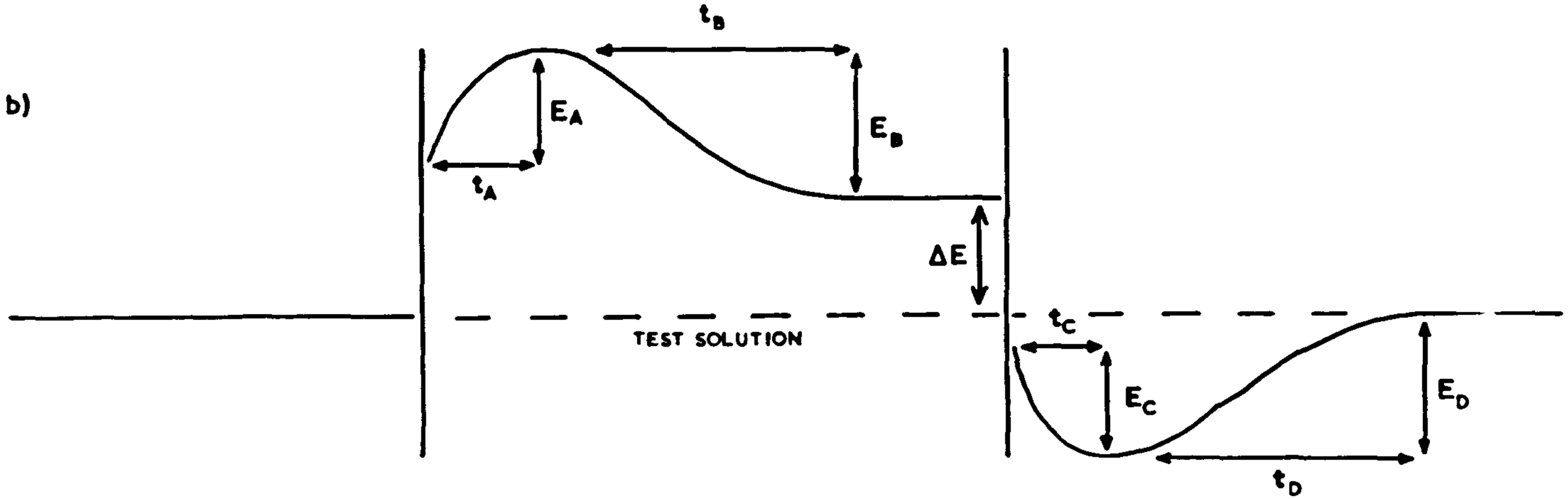


Fig. 28 THE RESPONSE OF SODA GLASS ELECTRODES IN ALKALINE SOLUTIONS AFTER TREATMENT WITH HCL OR HBr

showed type D_1 response in alkaline solutions after treatment with HCl, but for the GG 33 electrodes this type of behaviour was sometimes modified by an initial rapid increase in error to give a transient of type C_2 as shown in figure 28b. An example of a typical result is illustrated in figure 29 where the e.m.f.-time variations observed during two experiments with the same electrode are plotted on the same scale. Further examples are given in table 9.3, and here as in all similar tables in this chapter the solutions for each electrode are listed in the order of testing.

In table 9.4, which gives details of results obtained with the Jena H electrode No. 21, it is seen that the effect was enhanced by repeated treatment with an HCl solution. This indicates either that the effect is increased by alternate immersion of the electrode in acid and alkaline solutions or simply that the magnitude of the increase in the alkaline error depends upon the time of contact with the HCl. As will be seen in the discussion, chapter 11, a quantitative correlation of these factors would require a more extensive investigation than has been possible here, with careful control of the numerous variables.

The change in the behaviour of a soda glass electrode as a result of treatment with HCl was found to be only semi-permanent and the electrode recovered its former response characteristics after a period of a week or more. The results in table 9.5 for electrodes Nos. 1 and 8 show that in both cases recovery was almost complete six days after the electrode had been tested in HCl. However it was found that when testing an electrode in alkaline

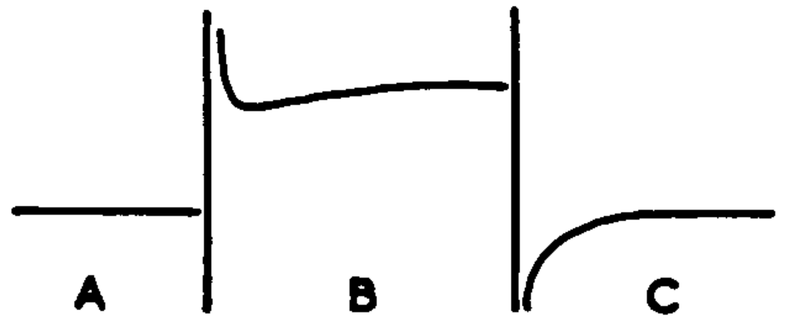
ELECTRODE No. 5

(E.I.L. GG 33)

11/5/65

BEFORE 0·5m HCl:

(TEST 79)



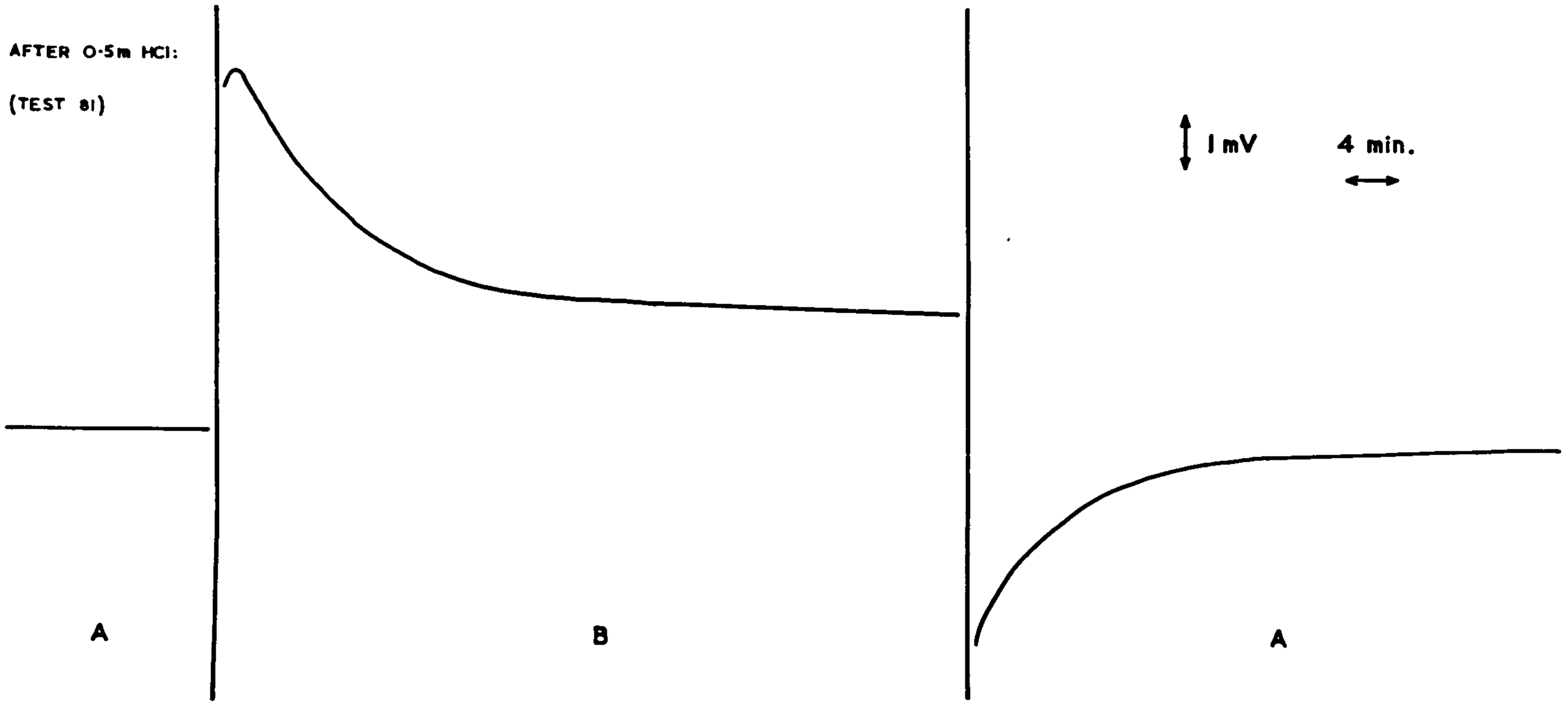
A. 0·1m Cl^- / Tris

B. 0·1m Cl^- / Tris + 1·0m NaCl

C. 0·1m H_2SO_4

AFTER 0·5m HCl:

(TEST 81)



1 mV

4 min.

Fig. 29 The Effect of HCl & HBr on the Response of Soda Glass Electrodes.

TABLE 9.3.

a) Electrode No. 5 (GG 33) 24/8/66

Solution	Test	Error	Transients			
		(mV)	Test Solution		Standard Solution	
1.0m Li^+ , p_wH 10.59	151	+3.7	0.5mV	D_1	1.9mV	D_1
0.5m HCl	152	-12.8				
1.0m Li^+ , p_wH 10.59	153	+9.8	4.8mV	C_2	1.9mV	C_2
			2.5mV		2.0mV	

b) Electrode No. 12 (GG 33) 17/8/65

Solution	Test	Error	Transients			
		(mV)	Test Solution		Standard Solution	
1.0m K^+ , p_wH 10.05	236	+4.7	2.5mV	D_1	1.5mV	D_1
0.5m HCl	237	-12.8				
1.0m K^+ , p_wH 10.05	238	+7.1	6.3mV	D_1	3.9mV	D_1

TABLE 9.4.

Electrode No. 21 (Jena H) 4/1/66

Solution	Test	Error	Transients (All type D_1)	
		(mV)	Test Solution	Standard Solution
1.0m Na^+ , p_wH 9.84	193	+3.6	1.0mV 1 min.	E Response
1.0m Na^+ , p_wH 9.84	194	+3.6	0.3mV 1 min.	E Response
1.0m HCl	195	-3.6		
1.0m Na^+ , p_wH 9.84	196	+4.2	4.2mV 20 min.	3.6mV 14 min.
1.0m HCl	197	-4.0		
1.0m Na^+ , p_wH 9.84	198	+4.8	5.6mV 27 min.	6.3mV 23 min.
1.0m HCl	199	-4.0		
1.0m Na^+ , p_wH 9.84	200	+5.8	9.2mV 50 min.	11.6mV 31 min.

TABLE 9.5.

a) Electrode No. 1. (GG 33)

Date	Solution	Test	Error	Transients	
			(mV)	Test Solution	Standard Solution
29/7/65	1.0m Na^+, p_wH 10.49	123	+15.2	2.0mV C_1	0.3mV C_1
	0.5m HCl	124	-6.0		
	1.0m HCl	125	-12.8		
	1.0m Na^+, p_wH 10.49	126	+21.8	10.9mV D_1	11.5mV D_1
4/8/65	1.0m Na^+, p_wH 10.49	133	+16.4	1.6mV C_1	0.4mV C_1

b) Electrode No. 8. (GG 33)

Date	Solution	Test	Error	Transients	
			(mV)	Test Solution	Standard Solution
11/5/65	1.0m Na^+, p_wH 8.83	75	+1.1	0.3mV C_1	E
	0.5m HCl	76	-2.9		
		77	-2.8		
	1.0m Na^+, p_wH 8.83	78	+2.0	0.5mV C_2 2.0mV	1.8mV D_1
17/5/65	1.0m Na^+, p_wH 8.83	82	+1.5	0.8mV C_1	0.7mV D_1
		83	+1.4	0.4mV C_1	E

solutions subsequent to treatment with HCl, the e.m.f.-time variations generally reverted to normal more rapidly than the magnitudes of the final errors, and this may also be seen from the data in table 9.5. For example, when electrode No. 1 was tested in alkaline sodium solutions on 4/8/65, it gave response of type C_1 similar to that observed on the earlier date before it was placed in the HCl. The error, on the other hand, although rather smaller than that observed immediately after the electrode was tested in HCl, was still a little larger than that originally observed during test 123. Similar observations may be made concerning the data for electrode No. 8 given in the same table. On account of the factors just discussed it was considered necessary when dealing with the data for the GG 33 electrodes in the last chapter to omit from table 8.2 (the magnitudes of the sodium errors under normal conditions) certain results included in the table of transients, table 8.3.

In order to investigate whether this effect could be brought about by any strong acid solution, irrespective of whether the glass electrode showed an error in it or not, 1 molal sulphuric acid was introduced into some of the experimental runs. Table 9.6 gives details of some results obtained with electrode No. 6, from which it may be seen that the sulphuric acid solution did not produce this effect even though it was more concentrated than the 0.5m HCl, which did. Caudle[1] suggested that molal sulphuric acid was particularly effective in reconditioning an electrode after the observation of an acid error. It was therefore thought possible that treatment of a

TABLE 9.6.

Electrode No.6. (GG 33) 21/5/65

Solution	Test	Error	Transients			
		(mV)	Test Solution		Standard Solution	
1.0m Na^+ , p_wH 8.83	96	+2.3	0.3mV 0.3mV	D_2	0.8mV	D_1
1.0m H_2SO_4	-	0.0				
1.0m Na^+ , p_wH 8.83	97	+2.2	Response E		1.0mV	D_1
0.5m HCl	98	-6.8				
1.0m Na^+ , p_wH 8.83	99	+3.2	1.9mV	D_1	2.2mV	D_1
	100	+3.1	0.2mV 0.5mV	C_2	1.3mV	D_1

soda glass electrode with this solution after testing in HCl, might result in a much more rapid recovery of its normal behaviour. This was investigated with electrode No. 12 which on one occasion (12/11/65) was placed in molal sulphuric acid for three hours after testing in HCl. However the effect of the HCl was still apparent when the electrode was again tested in an alkaline solution at the end of this period (Test 163).

It was now of interest to determine whether this effect is produced by immersing a glass electrode in any acid solution in which it shows an error or whether it is peculiar to HCl. Experiments were therefore carried out in which the HCl was replaced by HBr solutions sufficiently concentrated to cause the electrodes to show errors, and it was found that these solutions had the same effect as the HCl for both the Jena H and the GG 33 electrodes. Some typical results are given in table 9.7.

The main features of the transients shown by the soda glass electrodes, when tested in alkaline solutions soon after treatment with concentrated HCl or HBr, are given in tables 9.8 and 9.9. The symbols in these tables correspond to those in figure 28 and in each case the electrode had been placed in a hydrochloric or hydrobromic acid solution in which it gave an error, earlier on the same day. Although most of the data in these tables refer to alkaline errors in the pH range 8 - 10.5, it may be seen that the effect was also observed in a sodium hydroxide-sodium chloride solution at pH 13 with electrode No. 12 (Test 160). However at this pH the increase in the error produced by immersion in HCl was small relative to the large error observed under normal circumstances.

TABLE 9.7.

Electrode No. 9. (Jena H) 22/12/65

Solution	Test	Error	Transients			
		(mV)	Test Solution		Standard Solution	
1.0m Li^+ , p_wH 10.74	188	+ 3.1	-0.5mV 0.3mV	D_2	Response E	
5.0m HBr	191	-14.2	10.7mV	C_1	2.1mV	D_1
1.0m Li^+ , p_wH 10.74	192	+ 4.6	2.9mV	D_1	3.8mV	D_1

Electrode No. 12. (GG 33) 21/12/65

Solution	Test	Error	Transients			
		(mV)	Test Solution		Standard Solution	
1.0m Na^+ , p_wH 9.84	179	+ 8.0	1.0mV	C_1	Response E	
1.0m Li^+ , p_wH 10.74	180	+ 5.7	0.6mV	C_1	0.6mV	D_1
5.0m HBr	181	-49.5 ($\pm$0.7)	31 ± 1mV	D_1	9 ± 2mV 0.4mV	D_2
1.0m Na^+ , p_wH 9.84	182	+11.0	9.5mV	D_1	11.6mV	D_1
1.0m Li^+ , p_wH 10.74	183	+ 8.4	3.3mV 1.1mV	C_2	0.6mV 3.0mV	C_2

TABLE 9.8.

Transients shown by E.I.L. GG 33 Electrodes in Alkaline Solutions after treatment with concentrated HCl or HBr

ΔE, E_A, E_B, E_C and E_D in mV. t_A, t_B, t_C and t_D in min.

Electrode No. 1

	Date	p_wH	Test	ΔE	E_A	t_A	E_B	t_B	E_C	t_C	E_D	t_D
1.0m Na^+	17/5/65	8.83	89	+3.0		D_1	3.2	50		D_1	2.9	18
	29/7/65	10.49	126	+21.8		D_1	10.9	60		D_1	11.5	60[x]
1.0m Li^+	17/12/65	10.74	175	+7.9		D_1	6.8	29		D_1	8.7	32

Electrode No. 5

	Date	p_wH	Test	ΔE	E_A	t_A	E_B	t_B	E_C	t_C	E_D	t_D
1.0m Na^+	11/5/65	8.83	81	+2.4	0.3	1	4.6	54		D_1	3.7	42
	29/7/65	10.49	131	+26.3	3.5	3	12.2	47	-		-	
1.0m Li^+	24/8/65	10.59	153	+9.8	4.8	12	2.5	68	1.9	8	2.0	52
	21/12/65	10.74	187	+10.5	1.7	2	4.2	34		D_1	9.2	32

[x] Estimated time, e.m.f.-time trace not followed at this point.

Table 9.8. (Cont.)

Electrode No. 6

	Date	p_wH	Test	ΔE	E_A	t_A	E_B	t_B	E_C	t_C	E_D	t_D
1.0m Na^+	19/5/65	8.83	93	+2.9	0.4	1	4.1	49	0.3	1	3.2	40[x]
	21/5/65	8.83	99	+3.2		O_1	1.9	29		O_1	2.2	20
	21/5/65	8.83	100	+3.1	0.2	2	0.5	17		O_1	1.3	12
	11/8/65	10.49	145	+18.2		O_1	4.7	31		O_1	6.8	45
1.0m Li^+	11/8/65	10.59	144	+6.4	1.5	3	1.1	37		O_1	2.6	20

Electrode No. 8

	Date	p_wH	Test	ΔE	E_A	t_A	E_B	t_B	E_C	t_C	E_D	t_D
1.0m Na^+	21/7/64	8.43	319	+0.9		O_1	3.2	12		O_1	2.3	16
	11/5/65	8.83	78	+2.0	0.5	1	2.0	16		O_1	1.8	17
1.0m K^+	17/8/66	10.05	232	+4.8		O_1	1.3	14		O_1	0.7	10

[x] Estimated time - e.m.f.-time trace not followed at this point.

TABLE 9.8. (Cont.)

Electrode No. 12

	Date	p_wH	Test	ΔE	E_A	t_A	E_B	t_B	E_C	t_C	E_D	t_D
1.0m Na^+	21/7/64	8.43	322	+1.8	D_1		4.2	12	1.1	½	1.5	14
	21/12/65	9.84	182	+11.0	D_1		9.5	31	D_1		11.6	31
	4/11/65	10.04	159	+13.7	0.8	1	4.2	27	D_1		5.2	45
	12/11/65	10.04	163	+11.8	0.9	2	0.6	14	D_1		1.1	12
	4/11/65	13.00	160	+115.5	0.4	1	4.5	25	0.9	1	7.9	40
1.0m Li^+	21/12/65	10.74	183	+8.4	3.3	2	1.1	26	0.6	1	3.0	23
1.0m K^+	17/8/66	10.05	238	+7.1	D_1		6.3	30	D_1		3.9	10

TABLE 9.9.

Transients shown by Jena H Electrodes in Alkaline Solutions after treatment with concentrated HCl or HBr

All transients of type D_1

ΔE, E_B and E_D in mV. t_B and t_D in minutes.

Electrode No. 9.

	Date	p_wH	Test	ΔE	E_B	t_B	E_D	t_D
1.0m Lithium	22/12/65	10.74	192	+4.6	2.9	17	3.8	12

Electrode No. 21

	Date	p_wH	Test	ΔE	E_B	t_B	E_D	t_D
1.0m Sodium	4/1/66	9.84	196	+4.2	4.2	20	3.6	14
	4/1/66	9.84	198	+4.8	5.6	27	6.3	23
	4/1/66	9.84	200	+5.8	9.2	50	11.6	31
	12/11/65	10.04	167	+4.7	1.0	5	2.2	7
1.0m Lithium	17/12/65	10.74	178	+4.0	3.2	14	-	-

It was noted earlier that the large transients observed during these experiments were either of type D_1 or C_2. The probability of observing type C_2 response rather than type D_1 appeared to become larger as the glass electrode recovered from the effect of the HCl or HBr. As the time between testing in the acid and testing in an alkaline solution was increased, the large decrease in the alkaline error became smaller and the initial increase appeared and became more prominent. For example if an electrode was tested twice in the alkaline solution type D_1 response might be observed the first time and C_2 the second as was found for electrode No. 6 on 21/5/65 (Tests 99 and 100 in table 9.6). Comparison of the two results for electrode No. 12 and sodium solution of p_wH 10.04, obtained during different experimental runs, shows that although type C_2 response was observed in both cases, when testing was delayed for three hours (Test 163), the second part of the transient (i.e. the decrease of e.m.f.) was much reduced. It was again observed that after treatment with acid solutions in which they gave errors, certain electrodes tended to show one type of response whereas some showed the other; for example electrode No. 5 usually gave type C_2 but electrode No. 1 always gave type D_1. This might indicate that some electrodes recover from the effect of HCl or HBr more rapidly than others but much more data would be required to make any firm conclusion.

It has already been pointed out that in the early stages of this investigation, 0.1m HCl was used as a standard solution. The soda glass electrodes tested during these experimental runs showed D_1 transients when

tested in alkaline solutions containing sodium ions and in the light of the subsequent results which have been discussed in this chapter, this indicates that the 0.1m HCl solution had some influence upon the electrode response. This factor makes it difficult to interpret these results but they have been tabulated in the appendix with the other data for future reference.

Finally experiments were carried out to determine whether this effect could also be produced by dilute hydrofluoric acid solution. A 0.1m sodium fluoride solution buffered to a pH of about 4.8 was used for this purpose. The solution also contained sodium chloride so that a silver-silver chloride electrode could be used as a check upon the hydrogen electrode. It was thought that the activity of hydrofluoric acid in this solution would be sufficient to cause errors of the soda glass electrodes but not large enough for the solution to attack the glass of the cell vessel. However even with such a dilute solution of hydrofluoric acid, experimental difficulties were encountered. It was found that the hydrogen - silver-silver chloride e.m.f. for a cell containing this solution, was not constant during an experimental run, but drifted to increasing values at the rate of about 1mV in 4 hours. After one experimental run a cell containing this solution was left overnight and the e.m.f. again measured the next day. It was found that the drift had continued during the night when the flow of hydrogen had been shut off, and hence it was not caused by the passage of the gas.

It is probable that this drift of e.m.f. was due to a change in the composition of the solution resulting from its interaction with the glass of

the cell vessel. Attack of the glass by hydrofluoric acid according to the reaction:

$$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$$

would produce an increase in the pH of the solution and this would cause the observed e.m.f. to increase also. This change in pH would mainly effect the potential of the hydrogen electrode, and on renewing the solution in the hydrogen electrode compartment of the cell, it was in fact found that the e.m.f. reverted to almost exactly its original value. Further evidence for this explanation was provided by the fact that when the cell was cleaned after the experimental run it was observed to show signs of etching. In subsequent runs with this solution attempts were made to prevent attack of the glass cell vessel by coating it with 'Repelcote' but this was not successful. The e.m.f. still drifted and the cell again showed signs of etching. It is possible that a stable e.m.f. would have been obtained if a cell could have been constructed using say teflon or polythene. However there was insufficient time to try this during the present investigation.

Nevertheless despite this experimental difficulty it was possible to obtain some useful results using this fluoride solution. In fact several electrodes were tested in the solution relative to the hydrogen electrode and apparently gave negative errors. Despite the instability of the hydrogen electrode potential there are two reasons for believing these errors to be genuine and not the result of incorrect functioning of the hydrogen electrode. First the e.m.f.:-

(Pt) H_2 | Solution | AgCl-Ag

was observed to be increasing whereas the e.m.f:-

(Pt) H_2 | Solution | Glass electrode

showed a negative deviation from the correct value. Hence the glass electrode errors were almost certainly larger than those actually observed. Secondly the e.m.f's. of the glass electrode cells showed time variations of the kind normally associated with the errors and completely different to the very slow drift of e.m.f. observed for the hydrogen - silver-silver chloride cell. Also there was no doubt that when the glass electrodes were treated with this solution it produced a change in their response characteristics. When presenting the results of experiments with the fluoride solution in the appendix, the errors actually observed have been quoted in order to indicate the time variation of the e.m.f. However the absolute magnitudes of the errors cannot be regarded as significant.

Two soda glass electrodes were tested in the fluoride solution, electrode No. 8 (E.I.L. GG 33) and electrode No. 21 (Jena H) and the data obtained are summarised in table 9.10. It can be seen that for these electrodes the treatment with dilute hydrofluoric acid produced the same effect upon the errors observed in alkaline solutions as did the other halogen acids investigated. In both cases the error observed in the borax buffer was larger after the electrode had been treated with the fluoride solution and large type D_1 transients were observed.

Four pH responsive glass electrodes, believed to have lithia glass membranes, were also tested in the fluoride solution. These were:

TABLE 9.10.

Electrode No. 8 (GG 33) 3/8/66

Solution	Test	Error	Transients					
			Test Solution			Standard Solution		
		(mV.)		mV.	min.		mV.	min.
1.0m Na^+, p_wH 9.16 (Borax)	218	+2.0	E	-	-	D_1	0.5	1
0.1m F^- (Acetate) approx. pH 4.8	219	-4.2[x]	C_2	0.8 0.3	1 8	D_1	1.7	4
1.0m Na^+, p_wH 9.16 (Borax)	220	+2.9	D_1	3.5	17	D_1	4.9	25

Electrode No. 21 (Jena H) 9/8/66

Solution	Test	Error	Transients					
			Test Solution			Standard Solution		
		(mV.)		mV.	min.		mV.	min.
1.0m Na^+, p_wH 9.16 (Borax)	222	+1.4	E	-	-	E	-	-
0.1m F^- (Acetate) approx. pH 4.8	223	-3.0[x]	C_1	0.7	15	D_1	0.6	2
1.0m Na^+, p_wH 9.16 (Borax)	224	+2.0	D_1	1.9	20	D_1	2.2	20

[x] Apparent error.

Electrode No. 4 (Radiometer B) Electrode No. 16 (Radiometer C)

Electrode No. 17 (Radiometer B) Electrode No. 22 (Jena HA)

It was found that the solution had much greater effect upon the Radiometer B and Jena HA electrodes than upon either the Radiometer C or soda glass electrodes. Details of the response shown by the Radiometer B and Jena HA electrodes in the fluoride solution and during subsequent experiments with other solutions are given in tables 9.11 to 9.13. It may be seen that when placed in the fluoride solution, each of these electrodes gave a negative error which in general showed a very rapid increase with time, corresponding to the decrease in e.m.f. indicated in each of the tables. The Jena HA electrode was left in the solution somewhat longer than the other two and it was found that the rapid decrease in e.m.f., which in this case lasted 14 minutes, was followed by a period during which the e.m.f. first of all increased at a slower rate, and then began to decrease again. Since the fluoride solution was apparently having a rather drastic effect upon these electrodes, they were not left in it for very long periods and in every case the e.m.f. was still changing when the electrode was transferred back to a standard solution. All three electrodes showed type C_1 response in the standard solution and for each one, comparison of the approximately constant final e.m.f. with the e.m.f. previously observed for a standard solution showed that the asymmetry potential had changed by about 8mV. This may be seen from the right hand column of each table which gives the final value of the calibration e.m.f. (E_7) observed for each solution or set of solutions in which the electrode was tested.

TABLE 9.11.

Electrode No. 22 (Jena HA) 3/8/66

Solution	observed e.m.f. variation		Final E_7 (Volts)
Standard	see appendix		0.4883
0.1m F^- (Acetate) approx. pH 4.8 Test 349	a) 1.4mV increase b) 25.7mV decrease c) 2.0mV increase d) 1.8mV decrease Apparent Error:- Initial -0.9mV Final -25.0mV	½ min. 13½ min. 7 min. 9 min.	
1.0m Na^+ (Acetate) p_wH 4.75	C_1 6.9mV increase	31 min.	0.4795 (decrease of 8.8mV)
1.0m Na^+ (borax) p_wH 9.16	C_1 5.4mV increase Error relative to acetate:- Initial +1.0mV Final +6.4mV	48 min.	
1.0m Na^+ (Acetate)	C_1 4.1mV decrease	10 min.	0.4790
0.1m H_2SO_4	Transient 0.4mV (Probably feature A) Instantaneous error:- -0.1mV	1 min.	0.4787
Standard Solutions	6 days later		0.4862

TABLE 9.12.

Electrode No. 4 (Radiometer B) 9/8/66

Solution	observed e.m.f. variation	Final E_7 (volts)
Standard	see appendix	0.6309
0.1m F^- (Acetate) approx pH 4.8 Test 350	a) 1.0mV decrease $\frac{1}{2}$ min. b) 0.2mV increase $1\frac{1}{2}$ min. c) 14.5mV decrease 11 min. Apparent Error:- Initial -0.4mV Final -15.7mV	
0.1mCl^-/Ethanolamine p_wH 10.29	C_1 3.6mV increase 28 min.	0.6229 (decrease of 8.0mV)
0.1m H_2SO_4	D_1 3.6mV increase 23 min. Error: Initial -4.5mV Final -0.9mV	0.6220
Standard Solutions	1 day later	0.6280

TABLE 9.13.

Electrode No. 17 (Radiometer B) 14/9/66

Solution	observed e.m.f. variation	Final E_7 (Volts)
Standard	see appendix	0.6274
0.1m F^- (Acetate) approx. pH 4.8 Test 351	C_1 27.1mV decrease 13 min. Apparent Error:- Initial -0.1mV Final -27.2mV	
a) 0.5mCl^-/Tris p_wH 8.15 (13 min.) b) 1.85m $MgSO_4$ (Tris) p_wH 8.43	C_1 7.6mV increase 64 min. Transfer after 13 min. - instantaneous error 0.0mV. Transient 0.5mV (Probably feature A)	0.6198 (decrease of 7.6mV)
0.1m H_2SO_4	a) 2.0mV decrease 6 min. b) 1.4mV increase 27 min. Initial Error:- -0.4mV	0.6186
0.5mCl^-/Tris p_wH 8.15	Instantaneous Error: 0.0mV Transient 0.6mV in 3 min. (Probably feature A)	0.6190

The glass electrodes were next transferred between solutions in which they had previously been error free within the precision of the experimental method, and it was found that their pH response had been considerably impaired. The Jena HA electrode, for example, showed a large positive error in the borax buffer relative to the acetate solution. This error was accompanied by large type C_1 transients both in the borax solution itself and after transfer back to the acetate solution. Of the Radiometer B electrodes, No. 4 was placed in an ethanolamine buffer after being tested in the fluoride solution and was then transferred to 0.1m H_2SO_4. Although this electrode had previously been error free in transfers between these two solutions, it now showed a negative error in the acid relative to the buffer solution. This error was initially 4.5mV but decreased to 0.9mV in 23 minutes. Electrode No. 17 on the other hand was transferred from the fluoride solution to a tris buffer and while the e.m.f. was still changing was further transferred to 1.85m $MgSO_4$ solution also buffered with tris. The e.m.f.-time variation observed for the latter solution was extrapolated to the instant of transfer, neglecting an initial rapid change (probably feature A), and the instantaneous error was found to be zero. The electrode was then transferred to 0.1m H_2SO_4 and although a rather rapid variation of e.m.f. was observed, the initial error was almost zero. On transfer to another standard solution, namely a tris buffer, extrapolation of the e.m.f.-time variation, neglecting a small initial transient (feqture A), again indicated zero instantaneous error.

The effect of the fluoride solution on the pH response of the Jena HA and Radiometer B electrodes may be summarised as follows. Electrode No. 17 was least affected and when transferred between solutions of widely different pH, showed small instantaneous or initial errors. However it did show unusually large variations of asymmetry potential. Electrodes Nos. 4 and 22 showed errors when transferred between standard solutions. Those observed for transfers of electrode No. 22 between the acetate and borax buffers might perhaps have been due to an alkaline error caused by the sodium ions in the latter. On the other hand this cannot be the explanation for the error observed when electrode No. 4 was transferred between 0.1m sulphuric acid and the ethanolamine buffer.

Electrodes Nos. 4 and 22 were also tested in standard solutions during subsequent experimental runs and were found to have recovered their normal pH response. Electrode No. 4 was observed to have recovered only one day after it had been in contact with the fluoride solution. Electrode No. 22 was not tested further until six days later, but its recovery may have been equally rapid. It was also found for both electrodes that the calibration e.m.f., although approximately constant during testing, had changed and was now nearer the value observed before testing the electrode in the fluoride solution.

It is interesting that the fluoride solution had least effect upon the Radiometer C electrode No. 16. In fact this electrode was apparently influenced less by the solution than were the two soda glass electrodes.

TABLE 9.14.

Electrode No. 16 (Radiometer C) 3/8/66

Solution	Test	Error	Transients					
			Test Solution			Standard Solution		
		(mV.)		mV.	min.		mV.	min.
1.0m Na^+, p_wH 9.16 (Borax)	69	+1.5	E	-	-	D_1	1.7	5
0.1m F^- (Acetate) approx. pH 4.8	352	-1.6[x]	D_2	0.6 0.7	½ 10	C_1	1.3	3
1.0m Na^+, p_wH 9.16 (Borax)	70	+1.7	D_1	1.2	2	D_1	1.5	7

[x] Apparent Error

In the fluoride solution itself it apparently showed a negative error and an e.m.f. variation similar in speed and magnitude to those observed for the soda glass electrodes. The pH response of the electrode was unimpaired by the treatment with this solution and if there was any effect upon the alkaline error it was very small. When the electrode was tested in the borax buffer after treatment with the fluoride solution, it showed a small type D_1 transient, whereas the response had previously been of type E. However this was not really significant since electrodes of this type showed both D_1 and E response under

normal circumstances. Furthermore the final constant e.m.f. showed an error only slightly larger than that previously observed for the borax buffer. The results of these experiments are summarised in table 9.14.

A qualitative explanation of the various effects observed during experiments with this fluoride solution will be advanced in Chapter 12. This will include consideration of the results obtained for both soda and lithia glass electrodes, and will also be extended to provide a possible explanation of the effect of the other halogen acids, upon the response of soda glass electrodes in alkaline solutions. In Chapter 11, some experiments for the further investigation of the latter effect are suggested, and the results obtained by Dole, Roberts and Holley[16] during experiments with a fluoride solution similar to the one used here, are considered in the light of the observations of the present work.

CHAPTER 10.

Experiments with Cation Selective Glass Electrodes

As was pointed out in section 3.3, the cation selective glass electrodes tested in this work were of the same types as those investigated by Mattock.[40,41] However, in the present work, a more refined testing procedure has been used and attention has been given to the time dependence of the glass electrode potentials. The experiments were designed for the examination of the following aspects of the electrode performance:

1. the response to changes of cation activity at approximately constant pH, for which solutions buffered with ethanolamine to a pH of about 10 were used; and

2. the effect of change of pH on the cation response.

This was tested using solutions of constant cation concentration (1.0m) and differing pH. All the solutions were buffered so that measurements could be made at constant and known pH values. The e.m.f.-time curves obtained were first of all examined to ascertain whether extrapolation to the instant of transfer, in the manner now well established for pH responsive electrodes, was possible. Secondly the reproducibility of the e.m.f. differences, shown by the electrodes on transfer between two cells, was investigated, and finally these e.m.f. differences were compared with theoretical values calculated using activity coefficient data from the literature. Also the pH response of two of the sodium selective electrodes was tested in acid solutions after they had been conditioned for a period in deionised water.

10.1. Sodium Selective Electrodes

Sodium Response: Three sodium selective electrodes were used in this work. Two of these, Nos. 24 and 26, were of type GEA 33 whereas the third, No. 23, was a GNA 33 electrode. The electrodes were tested in the following solutions containing sodium ions:

0.1m Cl^-/Ethanolamine + 0.01m NaCl, p_wH 10.09

0.1m Cl^-/Ethanolamine + 0.1m NaCl, p_wH 10.31

0.1m Cl^-/Ethanolamine + 1.0m NaCl, p_wH 10.55

0.1m Cl^-/Tris + 1.0m NaCl, p_wH 9.04 and 9.14

0.05m Borax + 0.9m NaCl, p_wH 9.16

0.1m Acetic acid, 0.1m Sodium Acetate + 0.9m NaCl, p_wH 4.75

0.01m HCl + 1.0m NaCl, p_wH 2.25

0.1m HCl + 1.0m NaCl, p_wH 1.23

Except for the solutions of low pH, i.e. the acetate buffer and the HCl - NaCl mixtures, the time variation of e.m.f. observed after transfer of a glass electrode to a new solution, was very very small and could be extrapolated to the instant of transfer just as readily as for the best pH responsive glass electrodes. The data are presented in tables 10.1 to 10.4; omitting those for the HCl - NaCl mixtures which will be given separately later, since the electrodes gave very large transients in these solutions. These tables are constructed on the same lines as those in section 6.1. for the pH responsive electrodes, and again zero time was taken as the moment of making the first e.m.f. measurement rather than the instant of transfer.

The observed differences (ΔE) between the e.m.f. for the solution in

TABLES 10.1 - 10.4 E.m.f. Data for Sodium Responsive Electrodes

E.m.f. values (volts) for cells:

glass electrode | Solution | AgCl - Ag

TABLE 10.1

Electrode No. 23 (GNA 33) 22/4/66

Initial Solution
$0.1m Cl^-/T$, $1.0m Na^+$, p_wH 9.04

Final e.m.f. -0.0931
(Constant 7 min.)

Solution	$0.1m Cl^-/E$ $1.0m Na^+$ p_wH 10.55	$0.1m Cl^-/E$ $0.1m Na^+$ p_wH 10.31	$0.1m Cl^-/T$ $1.0m Na^+$ p_wH 9.04	$0.01m HCl$ $1.0m Na^+$ p_wH 2.25	$0.1m Cl^-/T$ $1.0m Na^+$ p_wH 9.04	$0.1m Cl^-/E$ $1.0m Na^+$ p_wH 10.55	$0.1m Cl^-/E$ $0.1m Na^+$ p_wH 10.31
Time(min.)							
0	-0.0938	+0.0040	-0.0929			-0.0936	+0.0042
1	-0.0934	+0.0040	-0.0929			-0.0930	+0.0042
2	-0.0934	+0.0040	-0.0929	See Table 10.7.	Final e.m.f. constant 10 min.	-0.0931	+0.0042
5	-0.0935	+0.0040	-0.0930			-0.0932	+0.0041
Final	-0.0935 (8)	+0.0040 (8)	-0.0930 (8)		-0.0927	-0.0933 (15)	+0.0041 (12)
ΔE(mV)	-0.4*	+97.5	-96.9			-0.3*	+97.5

TABLE 10.2

Electrode No. 23 (GNA 33) 12/8/66

Initial Solution
0.1m Cl^-/T, 1.0m Na^+, p_wH 9.14

Final e.m.f. -0.0926
(0.2mV increase in 7 min.)

Solution	Borax 1.0m Na^+ p_wH 9.16	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14	Acetate 1.0m Na^+ p_wH 4.75	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14	0.1m HCl 1.0m Na^+ p_wH 1.23	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14	0.1m Cl^-/E 0.01m Na^+ p_wH 10.09
Time(min.)							
0	-0.0859	-0.0925	-0.0884	-0.0921			+0.0767
1	-0.0859	-0.0925	-0.0880	-0.0922	See Table 10.7	Final e.m.f. Constant 8 min.	+0.0767
2	-0.0859	-0.0925	-0.0879	-0.0923			+0.0767
5	-0.0859	-0.0925	-0.0878	-0.0924			+0.0767
Final	-0.0859 (7)	-0.0925 (8)	-0.0878 (10)	-0.0924 (11)		-0.0923	+0.0767 (8)
ΔE(mV)	+6.7	-6.6	+4.7*	-4.6*			+169.0

TABLE 10.2. (Cont.)

Electrode No. 23 (GNA 33) 12/8/66.

Solution	0.1mCl^-/T 1.0m Na^+ p_wH 9.14	Acetate 1.0m Na^+ p_wH 4.75	0.1mCl^-/T 1.0m Na^+ p_wH 9.14
Time(min.)			
0	-0.0922	-0.0890	-0.0915
1	-0.0922	-0.0882	-0.0919
2	-0.0922	-0.0880	-0.0920
5	-0.0923	-0.0879	-0.0921
Final	-0.0923 (9)	-0.0878 (11)	-0.0922 (10)
ΔE(mV)	-168.9	+4.5*	-4.4*

TABLE 10.3.

Electrode No. 24. (GEA 33) 22/4/66

Initial Solution
0.1m Cl^-/T, 1.0m Na^+, p_wH 9.04

Final e.m.f. -0.1131
(Constant 7 mins.)

Solution	0.1m Cl^-/E 1.0m Na^+ P_wH 10.55	0.1m Cl^-/E 0.1m Na^+ p_wH 10.31	0.1m Cl^-/T 1.0m Na^+ p_wH 9.04
Time (min.)			
0	-0.1133	-0.0164	-0.1131
1	-0.1135	-0.0160	-0.1128
2	-0.1135	-0.0160	-0.1129
5	-0.1135	-0.0160	-0.1129
Final	-0.1135 (9)	-0.0160 (8)	-0.1129 (8)
E(mV)	-0.4*	+97.5*	-96.9*×

Electrode No. 24 (GEA 33) 12/8/66

Initial Solution
0.1m Cl^-/T, 1.0m Na^+, p_wH 9.14

Final e.m.f. -0.0972
(0.2mV decrease in 11 min.)

Solution	Borax 1.0m Na^+ p_wH 9.16	Acetate 1.0m Na^+ p_wH 4.75
Time(min.)		
0	-0.0906	-0.0933
1	-0.0906	-0.0929
2	-0.0906	-0.0928
5	-0.0906	-0.0928
Final	-0.0906 (7)	-0.0928 (7)
E(mV)	+6.6	-2.2*

× The electrode was then tested in 0.01m HCl, 1.0m Na^+, p_wH 2.25. See Table 10.8.

TABLE 10.4

Electrode No. 26 (GEA 33) 12/8/66 (1)

Initial Solution
Acetate, 1.0m Na^+, p_wH 4.75

Final e.m.f. -0.0986
(Constant 11 min.)

Solution	0.1mCl^-/T 1.0m Na^+ p_wH 9.14	0.1mCl^-/E 0.01m Na^+ p_wH 10.09	0.1mCl^-/T 1.0m Na^+ p_wH 9.14	Borax 1.0m Na^+ p_wH 9.16	Acetate 1.0m Na^+ p_wH 4.75	0.1mCl^-/T 1.0m Na^+ p_wH 9.14	Acetate 1.0m Na^+ p_wH 4.75
Time (min.)							
0	-0.1024	+0.0664	-0.1028	-0.0961	-0.0997	-0.1026	-0.0998
1	-0.1027	+0.0664	-0.1028	-0.0961	-0.0991	-0.1028	-0.0991
2	-0.1028	+0.0664	-0.1028	-0.0961	-0.0989	-0.1029	-0.0989
5	-0.1028	+0.0664	-0.1028	-0.0962	-0.0988	-0.1029	-0.0989
Final	-0.1028 (8)	+0.0664 (10)	-0.1028 (8)	-0.0962 (8)	-0.0988 (10)	-0.1029 (10)	-0.0989 (10)
ΔE(mV)	-4.2	+169.2	-169.2	+6.7	-2.7*	-4.1*	+4.0*

TABLE 10.4. (Cont.)

Electrode No. 26 (GEA 33) 12/8/66 (2)

Initial Solution
0.1m Cl^-/T, 1.0m Na^+, p_wH 9.14

Final e.m.f. -0.1089
(0.1mV increase in 9 min.)

Solution	Acetate 1.0m Na^+ p_wH 4.75	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14	Borax 1.0m Na^+ p_wH 9.16	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14	0.1m Cl^-/E 0.01m Na^+ p_wH 10.09	0.1m Cl^-/T 1.0m Na^+ p_wH 9.14
Time (min.)						
0	-0.1046	-0.1085	-0.1021	-0.1085	+0.0604	-0.1083
1	-0.1044	-0.1087	-0.1021	-0.1086	+0.0605	-0.1085
2	-0.1044	-0.1087	-0.1021	-0.1087	+0.0605	-0.1085
5	-0.1043	-0.1087	-0.1021	-0.1087	+0.0605	-0.1085
Final	-0.1043 (8)	-0.1087 (7)	-0.1021 (8)	-0.1087 (8)	+0.0605 (8)	-0.1085 (9)
ΔE(mV)	+4.6*	-4.4*	+6.6	-6.6*	+169.1	-169.0*

Between these two sets of experiments the electrode was tested in 0.1m HCl, 1.0m Na^+, p_wH 1.23 See Table 10.8

question and the final e.m.f. for the previous solution are given on the bottom line of each table, and except where these are marked with an asterisk they refer to the instant of transferring the electrode between the two solutions. It will be observed that in many of these cases, the e.m.f. remained constant to 0.1mV for between 5 and 10 minutes. Hence although extrapolation to the instant of transfer was possible, it was not really necessary since the extrapolated value would be the same to 0.1mV as that observed some minutes later. However, extrapolation would probably be essential in work of greater precision.

For the tests where ΔE is marked with an asterisk, the values refer to the final constant e.m.f. for the solution in question. This procedure was necessary for all electrodes when transferred to or from the acetate buffer, and as will be explained later, the transients observed after transfers involving this solution are believed to be due to interference by the hydrogen ion. However, in a few cases some very small transients were observed when an electrode was transferred between two solutions of higher pH, but comparison with the behaviour of pH responsive glass electrodes suggested that these transients were electrical rather than electrochemical in origin (i.e. feature A). One of these small transients was usually followed by a constant e.m.f. and hence the procedure of taking this final value was equivalent to extrapolating to the instant of transfer neglecting the transient. However, since the experimental method did not involve direct measurements against another sodium responsive electrode, it was impossible

to know whether this was the correct procedure for estimating the e.m.f. difference between two glass electrode cells. Nevertheless, the values obtained in this way showed good agreement with those from other tests and the uncertainty involved was not usually significant with the present experimental technique. It can be seen from the tables that except for the acetate buffer, the e.m.f. differences were in fact very reproducible, both for repeated testing of individual electrodes and from one electrode to another. The values obtained will therefore now be compared with those calculated from literature activity coefficient data.

As was pointed out in section 3.2, the values of ΔE, such as are listed in tables 10.1 to 10.4, are the e.m.f's. of concentration cells:

Ag-AgCl	NaCl (m_1) Solution 1	glass electrode	-	glass electrode	NaCl (m_2) Solution 2	AgCl-Ag

If the glass electrode shows the theoretical response to sodium ion activity, the values of ΔE will be equal to the e.m.f's. predicted by the equation

$$E = 2 \times 2.303 \frac{RT}{F} \log \frac{m_1 \gamma_1}{m_2 \gamma_2}$$

where γ_1 and γ_2 are the mean ionic activity coefficients of the sodium chloride solutions. Since mean ionic activity coefficient data for NaCl in buffer solutions are not available, the e.m.f's. were estimated using activity coefficients of unbuffered sodium chloride solutions from the literature. In each case it was assumed that the activity coefficient of NaCl in the buffer would be the same as that for the unbuffered solution of the same total ionic

strength. This seemed a reasonable assumption since in every case either the only cation present at significant concentration was sodium, or the only anion was chloride. The data were obtained during two experimental runs both of which involved a tris buffer containing 1.0m NaCl. These two tris buffers were chosen as reference solutions, since although they were not identical, they only differed by 0.1 of a p_wH unit in a region where variation of pH has little if any effect upon the electrode response. Hence, presenting the data in terms of the above concentration cell, solution 1 was always 1.0m NaCl buffered with tris and any deviation shown by the glass electrode was expressed as an error in the other solution. Thus if the observed e.m.f. was smaller than the estimated one, then the glass electrode was considered to show a positive error in the other solution. If on the other hand, the e.m.f. was larger than predicted then the glass electrode error was regarded as negative.

Since Lanier has pointed out the existence of discrepancies between values for the activity coefficients of NaCl given by three different sources, the e.m.f. values have been calculated using each of the three sets of data. The ionic strengths of the solutions, the activity coefficients and the e.m.f's. are given in table 10.5. As anticipated from the observations of Lanier, the differences are small for the low NaCl concentrations investigated in this work, and since the values of Robinson and Stokes lie between those of the other two sources they have been used for comparison with the experimental results.

TABLE 10.5.

(i) Activity Coefficients of NaCl Solutions

Solution	Ionic Strength	Molal Activity Coefficient		
		1	2	3
a) 0.1m Cl^-/Tris + 1.0m NaCl 0.1m Cl^-/Ethanolamine + 1.0m NaCl 0.1m KCl + 1.0m NaCl	1.10	0.651	0.655	0.656
b) 0.01m HCl	1.01	0.652	0.657	0.661
c) 0.1m Acetate + 0.9m NaCl 0.05m Borax + 0.9m NaCl	1.0	0.652	0.657	0.661
d) 0.1m Cl^-/Ethanolamine + 0.1m NaCl	0.2	0.727	0.735	0.738
e) 0.1m Cl^-/Ethanolamine + 0.01m NaCl	0.11	0.773	0.778	0.781

(ii) Calculated E.m.f. Values for NaCl Concentration Cells

Solution 1 0.1m Cl^-/Tris + NaCl

Solution 2	Calculated E.m.f. (mV)		
	1	2	3
a) 0.1m Cl^-/Ethanolamine + 1.0m NaCl 0.1m HCl + 1.0m NaCl	0.0	0.0	0.0
b) 0.01m HCl + 1.0m NaCl	+2.1	+2.0	+1.9
c) 0.1m Acetate + 0.9m NaCl 0.05m Borax + 0.9m NaCl	+5.1	+5.0	+4.8
d) 0.1m Cl^-/Ethanolamine + 0.1m NaCl	+97.3	+97.0	+96.9
e) 0.1m Cl^-/Ethanolamine + 0.01m NaCl	+168.7	+168.6	+168.5

1. Harned and Nims[53]
2. Robinson and Stokes[55]
3. Scatchard et. al.[54]

In table 10.6 are given the observed values of ΔE for the experiments where extrapolation of the e.m.f.-time variation to the instant of transfer was possible, including those where transients believed to be of type A have been neglected. The table also includes the deviations from the calculated values which are presented as a glass electrode error in solution 2. It can be seen that, except for the borax buffer, the estimated and observed values do not differ by more than about 0.01 of a pNa unit. Furthermore the values obtained with the different glass electrodes agree with each other more closely than with the calculated values. Hence it is probable that the differences between the observed and calculated e.m.f's. are due to the assumption involved in obtaining the activity coefficient values. The largest deviation was found with the borax buffer. However, owing to the presence of complex species, the assumption is perhaps least likely to be valid for this solution. The data for the solutions containing different concentrations of NaCl, indicate that within the precision of the method of testing, the glass electrodes show the theoretical response to change in sodium ion activity. The error in the ethanolamine containing 1.0m NaCl is somewhat surprising since tris and ethanolamine are rather similar in nature both being organic bases. However, the error was small and might also have been due to a difference in the NaCl activity coefficients for the two solutions. Clearly it will be necessary to carry out experiments with glass and sodium amalgam electrodes in order to resolve these differences.

When the glass electrodes were tested in sodium solutions of lower pH,

TABLE 10.6

Observed E.m.f. Values (ΔE) of NaCl Concentration Cells (mV)

Solution 1 - 0.1m Cl^-/Tris + 1.0m NaCl
p_wH 9.04 or 9.14

Solution 2.			GNA 33 Electrode		GEA 33 Electrodes.		
Buffer	p_wH	m_{Na^+}	No.23	Error	No.24	No.26	Error
0.1m Cl^- Ethanolamine	10.55	1.0	-0.4 -0.3	+0.4 +0.3	-0.4		+0.4
Borax	9.16	1.0	+6.7 +6.6	-1.7 -1.6		+6.7 +6.6 +6.6	-1.7 -1.6 -1.6
					+6.6		-1.6
0.1m Cl^- Ethanolamine	10.31	0.1	+97.1* +96.9 +97.2*	-0.1 +0.1 -0.2	+97.1* +96.9		-0.1 +0.1
0.1m Cl^- Ethanolamine	10.09	0.01	+169.0 +168.9	-0.4 -0.3		+169.2 +169.2 +169.1 +169.0	-0.6 -0.6 -0.5 -0.4

* These results were obtained by glass electrode transfers either to or from 1.0m NaCl buffered with ethanolamine (p_wH 10.55). They have been corrected to allow for the e.m.f. difference observed for transfers between this solution and Solution 1.

transients were observed which prevented application of the extrapolation procedure. These transients were obtained both when an electrode was transferred to one of these solutions and after it was transferred back to a sodium solution of higher pH. For experiments involving the acetate buffer they were usually small but on the other hand those associated with tests of the electrodes in the HCl - NaCl solutions were particularly large. The latter are presented in tables 10.7 and 10.8 in which are listed values of

ΔE, the difference between the e.m.f.:

glass electrode | NaCl | AgCl-Ag

observed at a given time during the experiment and that previously observed for the tris buffer. This procedure has been used both for the transient observed with the electrode in the HCl - NaCl solution and that observed after subsequent transfer back to the tris. Hence the final ΔE value for the tris buffer is a measure of the overall change in asymmetry potential, and the values for the HCl - NaCl solutions correspond to the concentration cell given earlier, with the HCl - NaCl mixture as solution 2. The latter may be compared with the calculated values in the manner already described, and the glass electrode errors corresponding to the final e.m.f's. for the HCl - NaCl solutions are also given on the last line of each teble.

Except for No. 26, the electrodes were transferred to the HCl - NaCl solutions directly from a tris buffer, and the e.m.f. difference, ΔE, was taken relative to the final e.m.f. observed for this solution immediately before transfer. Electrode No. 26 however, was transferred from the acetate

TABLE 10.7.

Response of Electrode No. 23 (GNA 33) in 1.0m Sodium Solutions of Low pH

a) 22/4/66.

Initial Solution
0.1mCl^-/T, 1.0m NaCl, p_wH 9.04

Solution	0.01m HCl 1.0m NaCl p_wH 2.25	0.1mCl^-/T 1.0m NaCl p_wH 9.04
Calculated ΔE (mV)	+2.0	-
Time (min.)	observed ΔE (mV)	
0	-16.0	+8.0
1	-7.5	+3.3
2	-5.6	+2.1
5	-3.5	+1.1
10	-2.3	+0.6
15	-1.8	+0.5
20	-1.5	+0.4
25		+0.3
30		+0.3
	-0.8 (50)	
Final	-0.7 (57)	+0.3 (32)
Final Error	+2.7	-

b) 12/8/66

Initial Solution
0.1mCl^-/T, 1.0m NaCl, p_wH 9.14.

Solution	0.1m HCl 1.0m NaCl p_wH 1.23	0.1mCl^-/T 1.0m NaCl p_wH 9.14
Calculated ΔE (mV)	0.0	-
Time (min.)	observed ΔE (mV)	
0	-29.3	+12.4
1	-21.3	+4.3
2	-18.8	+2.7
5	-15.8	+1.3
10	-14.1	+0.7
15	-13.3	+0.4
20	-12.7	+0.3
25	-12.4	+0.2
30	-12.1	
35	-11.9	
	-11.6 (51)	
	-11.5 (55)	
	-11.4 (60)	
Final	-10.9* (3 hrs.)	+0.1× ($2\frac{1}{2}$ hrs.)
Final Error	+10.9	-

* E.m.f. constant to 0.1mV for 10. min.

× E.m.f. constant to 0.1mV for 8 min.

TABLE 10.8.

Response of GEA 33 Electrodes in 1.0m Sodium Solutions of Low pH

Electrode No. 24 22/4/66.

Initial Solution
0.1mCl^-/T, 1.0m NaCl, p_wH 9.04

Solution	0.01m HCl 1.0m NaCl p_wH 2.25	0.1mCl^-/T 1.0m NaCl p_wH 9.04
Calculated E(mV)	+2.0	-
Time (min.)	observed	ΔE(mV)
0	-14.1	+10.1
1	-10.2	+5.3
2	-8.3	+3.8
5	-6.0	+2.2
10	-4.5	+1.4
15	-3.7	+1.0
20	-3.3	+0.8
25	-2.9	
30	-2.6	
35	-2.4	
40	-2.2	
45	-2.1	+0.1
50	-1.9	
55	-1.8	
60	-1.7	
Final	-1.7 (64)	+0.1 (50)
Final Error	+3.7	-

Electrode No. 26 12/8/66.

Initial Solution
Acetate, 1.0m NaCl, p_wH 4.75

Solution	0.1m HCl 1.0m NaCl p_wH 1.23	0.1mCl^-/T 1.0m NaCl p_wH 9.14
Calculated E(mV)	0.0	-
Time (min.)	observed	ΔE(mV)
0	-57.7	-5.5
1	-56.1	-9.8
2	-54.2	-10.7
5	-50.5	-10.9
10	-47.2	-10.3
15	-45.2	-9.6
20	-43.8	
25	-42.7	Minimum Value -11.0mV (4 min.)
30	-41.8	
35	-41.1	
40	-40.4	
45	-39.9	-7.6
50	-39.4	-7.4
55	-39.0	
60	-38.6	
Final	-37.1 (85) -36.1 (100) -34.7* (3 hours)	-6.0× (2 hours)
Final Error	+34.7	-

* Value changed from -34.8mV in 9 min.

× Value changed from -6.1mV in 9 min.

buffer, in which it showed a small error relative to the tris. The e.m.f. differences for this electrode were therefore taken relative to the final e.m.f. for the tris buffer immediately before transfer to the acetate. The change of e.m.f. observed in the intervening period for the acetate buffer however, was only 0.3mV, which was negligible compared to the magnitude of the error subsequently observed for the HCl - NaCl solution.

In each test the electrodes showed a positive error in the HCl - NaCl solution, and the error decreased continuously until an approximately constant final value was attained. In every case the electrode was transferred directly back to the tris buffer, and with the exception of the test for electrode No. 26, a continuously decreasing error was also observed for this solution (i.e. D_1 response in both solutions). Electrode No. 26 on the other hand, gave a type D_2 e.m.f.-time variation in the tris buffer, and the approximately constant final value showed that there had been an overall change of asymmetry potential of 6mV.

The essential features of these transients are given in table 10.9 together with the differences, ΔE_f, between the approximately constant final e.m.f. for the glass electrode cell containing the solution of low pH, and the e.m.f. for the electrode in the sodium solution buffered with tris. With the exception of the test of electrode No. 26 in the solution of p_wH 1.23, the latter have been taken as the average of the steady values observed before and after transfer to the solution under consideration. Hence the values of ΔE_f may be regarded as accurate to $\pm$0.2mV, although in some cases they

TABLE 10,9.

Errors and Transients of Sodium Responsive Electrodes

Experiments with 1,0m Sodium Solutions of Low pH

Concentration Cell - Solution 1. $0.1m Cl^-$/Tris + 1.0m NaCl

Electrode No. 23 (GNA 33)

Solution 2. p_wH	Buffer	ΔE_f	Error	D_1 Transients Solution 2.		Tris Buffer	
		mV	mV	mV	min.	mV	min.
4.75	Acetate	+4.6	+0.4	0.6	4	0.3	5
		+4.4	+0.6	1.1	5	0.7	7
2.25	0.01m HCl	-0.8	+2.8	15.3	57	7.7	22
1.23	0.1m HCl	-11.0	+11.0	18.4	3 hrs.	12.2	25

Electrode No. 24 (GEA 33)

Solution 2. p_wH	Buffer	ΔE_f	Error	D_1 Transients Solution 2.		Tris Buffer	
		mV	mV	mV	min.	mV	min.
4.75	Acetate	+4.4	+0.6	0.5	3*	-	-
2.25	0.01m HCl	-1.8	+3.8	12.4	64	10.0	40×

* Transferred from Borax Buffer.

× Estimated value, e.m.f. variation not followed at this point.

TABLE 10.9. (Cont.)

Electrode No. 26 (GEA 33)

Solution 2		ΔE_f	Error	D_1 Transients			
				Solution 2		Tris Buffer	
p_wH	Buffer						
		mV	mV	mV	min.	mV	min.
4.75	Acetate	+4.2	+0.8	-	-	0.4	4
		+4.1	+0.9	0.9*	5	0.3	2
		+4.0	+1.0	0.9	3	Transferred to 1.0m Na^+ p_wH 1.23	
		+4.5	+0.5	0.3	3	0.2	2
1.23	0.1m HCl	-34.7	+34.7	23.0×	3 hrs.	5.5	4
		-28.7	+28.7			5.0	2 hrs.
						(D_2 Transient)	

* Transferred from Borax Buffer.

× Transferred from Acetate Buffer

could have been specified with greater precision. For the above mentioned test of electrode No. 26, two values of ΔE_f have been given. This is due to the large variation of asymmetry potential during the period of this experiment and the two values are the errors relative to the different e.m.f's. in the tris before and after transfer to the HCl - NaCl solution. The glass electrode errors relative to the tris buffer, indicated by the two values of ΔE_f, are also given in table 10.9.

In view of the observations of previous investigators reviewed in chapter 3, it is almost certain that the errors and transients obtained when the electrodes were tested in the HCl - NaCl solutions, were due to interference by the hydrogen ion. The deviations between the observed and calculated values of ΔE_f for the acetate buffer were probably also due to hydrogen ion errors of the glass electrode, but these errors were so small that it is possible they were really due to failure of the assumption used in obtaining the activity coefficients. However, there are three reasons why the latter explanation seems improbable.

1. The e.m.f. differences observed on transferring a glass electrode to this solution, were less reproducible than those obtained for the solutions already considered in table 10.6.

2. The errors shown by the GEA 33 electrodes were larger than those for the GNA 33 electrodes, and this corresponds to the larger errors observed for the GEA 33 electrodes in the HCl - NaCl solutions.

3. The electrodes gave type D_1 e.m.f.-time curves which were similar to

the response shown during experiments with the HCl - NaCl solutions, but on a much smaller scale.

pH Response: In addition to the investigation of the response to sodium ions, the pH response was examined for electrodes Nos. 23 and 24. The testing procedure and the method of presenting the results, which are given in tables 10.10 and 10.11, were the same as those used for the pH responsive glass electrodes. The electrodes gave some transients which were apparently of type A, and the values of ΔE are those obtained by extrapolating the e.m.f.-time variations to the times of transfer neglecting these transients. Electrode No. 23 was error free in transfers between solutions of the two acids at the same molality, but gave errors when transferred between a 0.1m and a 1.0m solution. It gave a positive error of approximately 1mV in the 0.1m solutions relative to the 1.0m and hence in this range it showed a response of only about 58mV per pH unit. It also gave a large transient and a positive error in a tris buffer of p_wH 8.68 which did not contain NaCl, but this might have been due to a response to the tris cation. The data for this test are to be found in table 10.13. Electrode No. 24 was only tested in acid solutions but in these it gave error free results including those for transfers between different acid concentrations.

At the end of these experiments the electrodes were transferred first to an HCl - NaCl solution, and then to a tris buffer containing NaCl. As was to be expected, large errors in the hydrogen ion response were observed, and

TABLE 10.10.

Electrode No. 23. (GNA 33) 14/4/66.

Solution	0.1m H_2SO_4	1.0m HCl	0.1m H_2SO_4	0.1m HCl	1.0m HCl	0.1m H_2SO_4	0.1m Cl^-/T p_wH 8.68
Time (min.)							
0	0.3574	0.3500*	0.3569	0.3546	0.3500*	0.3559	
1	0.3574	0.3559	0.3559	0.3558	0.3550	0.3553	See Table 10.13
2	0.3573	0.3559	0.3559	0.3559	0.3551	0.3554	
5	0.3571	0.3558	0.3559	0.3559	0.3550	0.3555	
Final	0.3569 (10)	0.3555 (13)	0.3559 (9)	0.3559 (9)	0.3549 (10)	0.3555 (10)	
ΔE(mV)	-	-0.8	+0.4	0.0	-0.7	+0.4	

* Approximate Value - rapid change of e.m.f.

The electrode was stored in deionised water between these experiments and those on 19/4/66.

TABLE 10.10 (Cont.)

Electrode No. 23. (GNA 33) 19/4/66.

Solution	0.1m H_2SO_4	1.0m H_2SO_4	1.0m HCl	1.0m H_2SO_4	1.0m HCl	1.0m H_2SO_4	0.1m H_2SO_4
Time (min.)							
0	0.3621	0.3610	0.3575	0.3583	0.3564	0.3580	0.3579
1	0.3620	0.3597	0.3587	0.3578	0.3574	0.3569	0.3574
2	0.3618	0.3595	0.3586	0.3578	0.3574	0.3569	0.3574
5	0.3613	0.3591	0.3584	0.3577	0.3573	0.3568	0.3575
Final	0.3607 (9)	0.3588 (8)	0.3582 (8)	0.3575 (10)	0.3572 (8)	0.3568 (8)	0.3575 (9)
ΔE(mV)	-	-1.0	0.0	-0.2	0.0	-0.3	+0.6

After these experiments the electrode was transferred to

1. 0.01m HCl + 1.0m NaCl p_wH 2.25
2. 0.1m Cl^-/Tris + 1.0m NaCl p_wH 9.04

(See Table 10.13)

TABLE 10.11.

Electrode No. 24. (GEA 33) 19/4/66.

Solution	1.0m H_2SO_4	1.0m HCl	1.0m H_2SO_4	0.1m H_2SO_4	1.0m H_2SO_4	0.1m H_2SO_4
Time (min.)						
0	0.4060	0.4020	0.4080	0.4044	0.4058	0.4062
1	0.4060	0.4052	0.4049	0.4046	0.4042	0.4040
2	0.4059	0.4052	0.4048	0.4045	0.4042	0.4040
5	0.4057	0.4051	0.4046	0.4045	0.4041	0.4040
Final	0.4054 (11)	0.4050 (8)	0.4045 (8)	0.4044 (8)	0.4040 (8)	0.4039 (9)
ΔE(mV)	-	0.0	0.0	+0.1	-0.1	0.0

After these experiments the electrode was transferred to

1. 0.01m HCl + 1.0m NaCl p_wH 2.25
2. 0.1m Cl^-/Tris + 1.0m NaCl p_wH 9.04

(See Table 10.13)

TABLE 10.12. Transfers of Sodium Responsive Electrodes from Acid Solutions to Sodium Solutions.

Electrode No. 23. (GNA 33)

Date	Solution	E_1 (volts)	E_2 (volts)	Final Error (pH Response)	E_3 (volts)	Final Error (Sodium Response)
14/4/66	1.0m HCl	0.2331	0.3552	See Table 10.10.	-0.1221	-
	0.1m HCl	0.3525	0.3559		-0.0034	-
19/4/66	1.0m HCl	0.2330	0.3570		-0.1240	
	0.01m HCl 1.0m NaCl p_wH 2.25	0.3547	0.4025 to 0.4427 C_1 40.2 mV in 83 min.	+ 85 mV	-0.0478 to -0.0880	-2.4 mV
	0.1m Cl^-/T 1.0m NaCl p_wH 9.04	0.7543	0.8270 to 0.8467 C_1 19.7 mV in 55 min.	+489 mV	-0.0727 to -0.0924	Reference Solution

Electrode No. 24 (GEA 33)

Date	Solution	E_1 (volts)	E_2 (volts)	Final Error (pH Response)	E_3 (volts)	Final Error (Sodium Response)
19/4/66	0.01m HCl 1.0m NaCl p_wH 2.25	0.3547	0.4423 to 0.4706 C_1 28.3 mV in 80 min.	+67 mV	-0.0876 to - 0.1158	-3.1 mV
	0.1m Cl^-/T 1.0m NaCl P_wH 9.04	0.7543	0.8435 to 0.8752 C_1 31.7 mV in 110 min.	+471 mV	-0.0892 to -0.1209	Reference Solution

TABLE 10.13.

Further Transients of Sodium Responsive Glass Electrodes

Transfers from 0.1m H_2SO_4 to a) Tris buffer without NaCl
b) 1.0m Sodium solutions

Electrode No. 23 (GNA 33)				Electrode No. 24 (GEA 33)	
Date	14/4/66	19/4/66		19/4/66	
Final E_2 for 0.1m H_2SO_4(volts)	0.3555	0.3575	-	0.4039	-
Solution	0.1mCl^-/T - p_wH 8.68	0.01m HCl 1.0m NaCl p_wH 2.25	0.1mCl^-/T 1.0m NaCl p_wH 9.04	0.01m HCl 1.0m NaCl p_wH 2.25	0.1mCl^-/T 1.0m NaCl p_wH 9.04
Time (min.)	E_2(volts)	E_2(volts)	E_2(volts)	E_2(volts)	E_2(volts)
0	0.4200	0.4025	0.8270	0.4423	0.8435
1	0.4416	0.4130	0.8330	0.4459	0.8514
2	0.4497	0.4187	0.8364	0.4481	0.8557
5	0.4618	0.4268	0.8408	0.4526	0.8616
10	0.4721	0.4326	0.8434	0.4571	0.8657
15	0.4774			0.4600	0.8678
20	0.4807		0.8453		0.8693
25	0.4830		0.8457		
30	0.4848	0.4395	0.8460	0.4648	
35	0.4862	0.4401		0.4659	
40	0.4878	0.4406			
45		0.4409			
50		0.4413	0.8466		
55		0.4416	0.8467		
60		0.4418			
65		0.4420			0.8737
70		0.4422		0.4700	0.8739
75		0.4424		0.4703	
80		0.4426		0.4706	
Final	0.4878(40)	0.4427(83)	0.8467(57)	0.4706(80)	0.8752(110)
Transferred to:	-	0.1mCl^-/T 1.0m NaCl p_wH 9.04	-	0.1mCl^-/T 1.0m NaCl p_wH 9.04	-

these were accompanied by large transients of type C_1, details of which are given in tables 10.12 and 10.13. In these tables the e.m.f's. E_1, E_2 and E_3 refer to the cells:

(Pt) H_2 (p)	solution	AgCl-Ag	E_1
(Pt) H_2 (p)	solution	glass electrode	E_2
glass electrode	solution	AgCl-Ag	E_3

where p is the partial pressure of hydrogen. Both E_1 and E_2 are the actual cell e.m.f's. and not the values corrected to one atmosphere of hydrogen. The glass electrode potentials were measured relative to the hydrogen electrodes and the values of E_3 were calculated from the observed values of E_2 using the relation $E_3 = E_1 - E_2$. The main features of the transients are summarised in table 10.12 whereas details of the time dependence of the observed e.m.f's. (E_2) are given in table 10.13. In table 10.12, the errors in the pH response of the electrodes, are the differences between the final values of E_2 for the test solutions, and those previously observed for the respective electrodes in 0.1m H_2SO_4 given at the top of table 10.13. Also the deviations in the sodium response quoted for the HCl-NaCl solution in the last column of the table, were calculated relative to the approximately constant final e.m.f. subsequently observed for the NaCl buffered with tris, in the manner described above. As was indicated in section 4.4, these experiments were carried out before those for the investigation of the sodium ion response and the electrodes were left in the tris buffer with added sodium chloride to condition them for the later work.

The changes in E_3 observed for the two electrodes with the 1.0m NaCl buffered with tris, corresponded to the type D_1 transients observed when the electrodes were transferred between the same solutions during the experiments to test their sodium response. It will be noticed that the final value of E_3 for each electrode in the 0.01m HCl + 1.0m NaCl p_wH 2.25, indicated a negative error of the glass electrode sodium response in that solution, relative to the final e.m.f. subsequently observed for the tris + NaCl. This is in contrast to the positive errors shown by the electrodes when they were transferred to this solution from the tris + NaCl, during the later experiments. However, it is probable that if the electrodes had been left in the HCl-NaCl solution for longer, their potentials would have changed until the errors became positive relative to the tris + NaCl. Hence the transients observed for each electrode in these two solutions in this experiment, appeared to be part of the same process; probably the replacement of hydrogen ions by sodium ions in the surface of the glass, which is believed to be necessary for the electrode to show a response to sodium ions.

Graphical Presentation of Data for the GNA 33 Electrode: Finally two features of the results for the sodium responsive electrodes have been presented graphically in figures 30 and 31 using the data for electrode No. 23. Figure 30 illustrates in the usual manner, the relationship between the pH and sodium functions of the electrode, and figure 31 shows the response to change

in sodium ion activity at a pH of about 10. In order to allow for differences in chloride ion concentration between the various solutions, it has been found convenient to define $E' = E_3 + 0.05916 \log m_{Cl^-}$ where E' and E_3 are both in volts. For solutions where E_3 showed a time variation, the approximately constant final value was taken.

As indicated in table 10.14, the data were obtained during four different experimental runs, two for investigation of the pH response and two for the sodium response, and the e.m.f's. have therefore been corrected to allow for changes of the glass electrode asymmetry potential. As can be seen from this table all the runs except the first included measurements with a tris buffer + 1.0m NaCl. The e.m.f. (-0.0924 volts) and the corresponding value of E'(-0.0900 volts) observed for this solution in both the second and fourth experimental runs, were taken as standard, and the e.m.f's. obtained in the other runs were corrected to these values. The first run had the 1.0m HCl solution in common with the second, and the e.m.f's. for this run were therefore corrected to the value for the 1.0m HCl for the second run.

In figure 30, E' is plotted against p_wH for solutions of constant sodium ion concentration (1.0m) and HCl solutions without added NaCl. In figure 31 it is plotted against p_wNa, defined as $-\log m_{Na^+} \gamma_{\pm NaCl}$, the activity coefficients being obtained in the manner already described. Measurement of the gradient of the latter graph indicates that the electrode response was 59mV per p_wNa unit.

TABLE 10.14.

Data for Electrode No. 23 (GNA 33) shown in Figures 30 and 31

a) Sodium Solutions b) HCl Solutions

Date	Buffer	p_wH	m_{Na^+}	m_{Cl^-}	Corrected E_3(volts)	E'(volts) $E_3+0.05916 \log m_{Cl^-}$)
14/4/66	0.1m HCl	1.21	-	0.100	-0.0053	-0.0645
	1.0m HCl	0.19	-	1.00	-0.1240	-0.1240
19/4/66	1.0m HCl	0.19	-	1.00	-0.1240	-0.1240
	0.1mCl^-/T	9.04	1.00	1.10	-0.0924	-0.0900
22/4/66	0.01m HCl	2.25	1.00	1.01	-0.0932	-0.0929
	0.1mCl^-/T	9.04	1.00	1.10	-0.0924	-0.0900
	0.1mCl^-/E	10.55	1.00	1.10	-0.0928	-0.0904
	0.1mCl^-/E	10.31	0.100	0.200	+0.0047	-0.0367
12/8/66	0.1m HCl	1.23	1.00	1.10	-0.1033	-0.1009
	Acetate	4.75	1.00	0.900	-0.0879	-0.0906
	0.1mCl^-/T	9.14	1.00	1.10	-0.0924	-0.0900
	0.1mCl^-/E	10.09	0.0100	0.110	+0.0766	+0.0199

Response to change in Sodium Ion Activity at pH 9-10.5

Buffer	p_wH	m_{Na^+}	$\gamma_{\pm NaCl}$	p_wNa	E'(Volts)
0.1mCl^-/Tris	9.04 9.14	1.00	0.655	0.37	-0.0900
0.1mCl^-/Ethanolamine	10.31	0.100	0.735	1.27	-0.0367
0.1mCl^-/Ethanolamine	10.09	0.0100	0.778	2.22	+0.0199

Fig. 30 ELECTRODE No. 23 (GNA 33)

DEPENDENCE OF RESPONSE UPON pH.

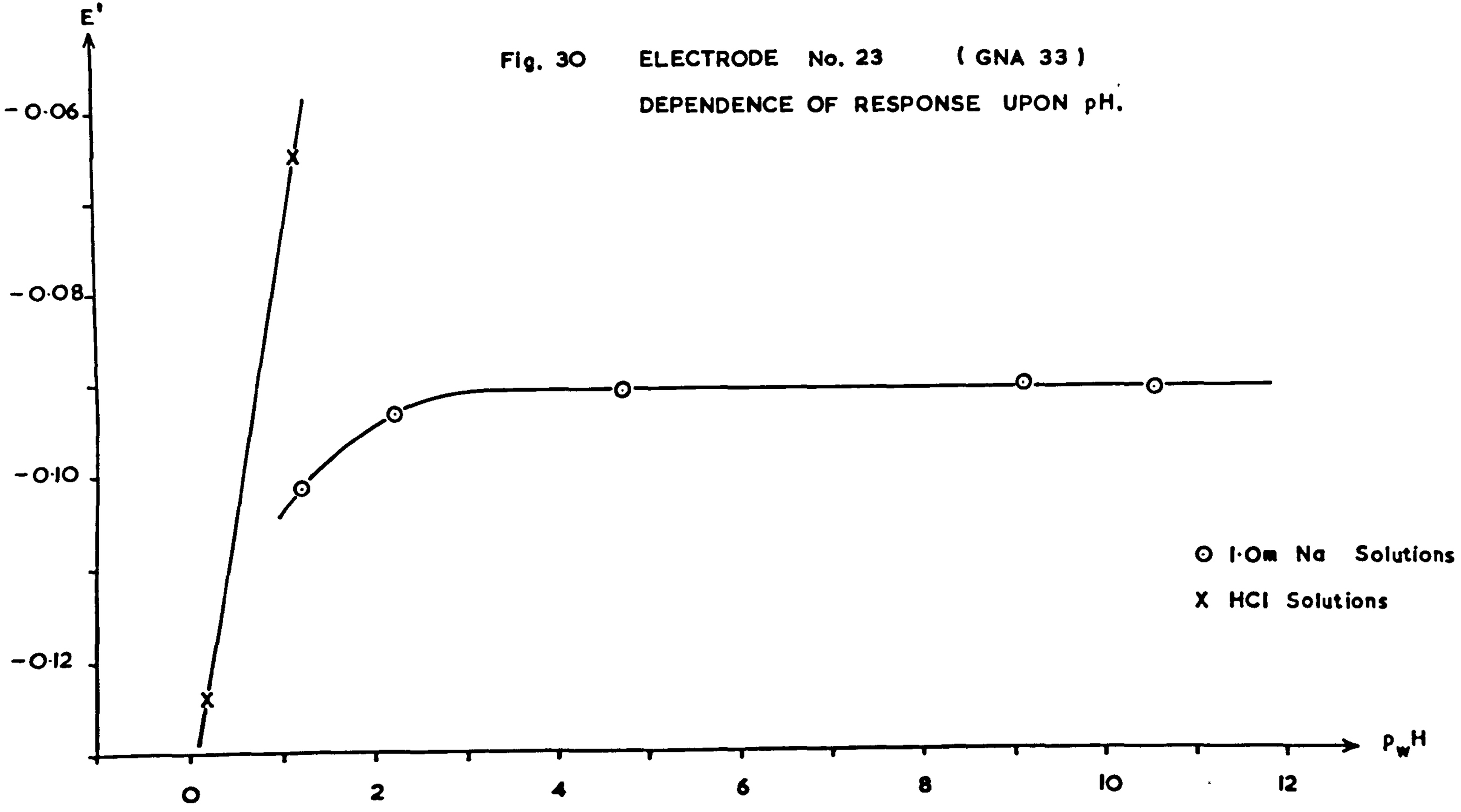
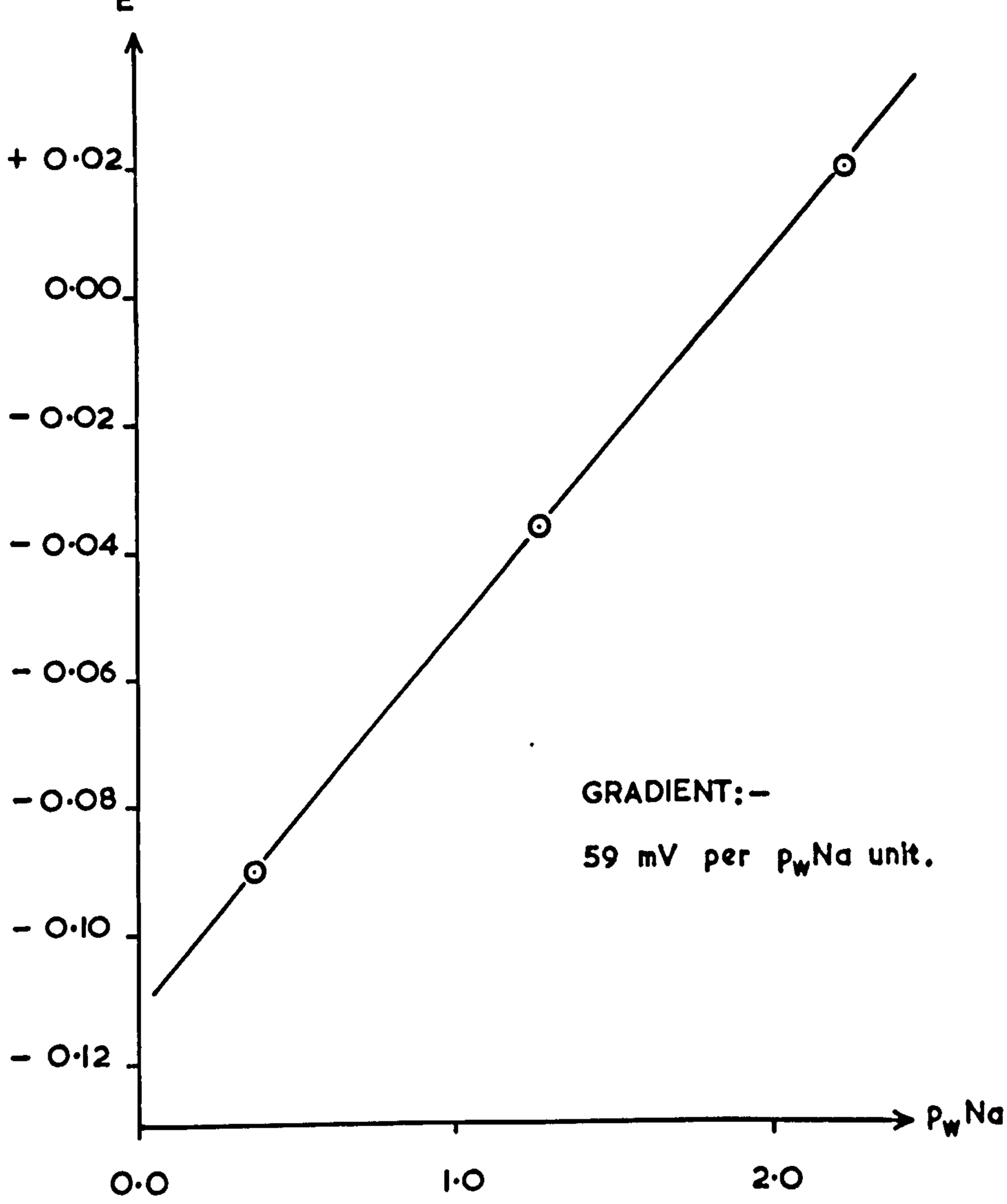


Fig. 31 ELECTRODE No. 23 (GNA 33)

RESPONSE TO CHANGE OF SODIUM ION ACTIVITY



GRADIENT:-

59 mV per p_wNa unit.

10.2. Potassium Selective Electrodes

Only two potassium selective electrodes were tested, Nos. 25 and 28, and both these were of type GKN 33. All the experiments were carried out on the same day, when the electrodes were tested in the following solutions:

0.1mCl^-/Ethanolamine + 0.1m KCl, p_wH 9.95

0.1mCl^-/Ethanolamine + 1.0m KCl, p_wH 10.05

0.1mCl^-/Tris + 1.0m KCl, p_wH 9.13

0.1m Acetic Acid, 0.1m Potassium Acetate + 0.9m KCl, p_wH 4.81

0.1m HCl + 1.0m KCl, p_wH 1.29

All the data obtained for transfers of the two glass electrodes between these solutions are presented in tables 10.15 and 10.16 in the same manner as has already been used for the sodium responsive electrodes.

For electrode No. 25 the e.m.f. observed immediately after transfer to a new solution, changed only slowly with time, even for experiments involving solutions of low pH. Hence in every case the e.m.f.-time variation could readily be extrapolated back to the instant of transfer, and the e.m.f. differences (ΔE) quoted for this electrode, were obtained by this procedure. The very slight transients sometimes observed during the first few moments after transfer have been neglected.

Electrode No. 28, on the other hand gave several transients of significant size, but these appeared to be random and unrelated to the nature of the solutions involved in the transfer. Although in several experiments the e.m.f.-time curve could have been extrapolated back to the instant of transfer,

TABLES 10,15 and 10,16. E,m,f, Data for Potassium Responsive Electrodes

E.m.f. Values (volts) for cells:

glass electrode | Solution | AgCl - Ag

TABLE 10,15

Electrode No, 25 (GKN 33) 6/9/66 (1)

Initial Solution
$0.1mCl^-/E$, 1.0m K^+, p_wH 10.05

Final e.m.f. -0.1034
(Constant 8 min.)

Solution	Acetate 1.0m K^+ p_wH 4.81	$0.1mCl^-/E$ 1.0m K^+ p_wH 10.05	$0.1mCl^-/E$ 0.1m K^+ p_wH 9.95	$0.1mCl^-/E$ 1.0m K^+ p_wH 10.05	$0.1mCl^-/T$ 1.0m K^+ p_wH 9.13	$0.1mCl^-/E$ 1.0m K^+ p_wH 10.05	$0.1mCl^-/E$ 0.1m K^+ p_wH 9.95
Time(min.)							
0	-0.0988	-0.1034	-0.0098	-0.1033	-0.1040	-0.1034	-0.0098
1	-0.0988	-0.1034	-0.0096	-0.1034	-0.1040	-0.1034	-0.0097
2	-0.0988	-0.1034	-0.0097	-0.1034	-0.1040	-0.1034	-0.0097
5	-0.0989	-0.1034	-0.0097	-0.1034	-0.1041	-0.1035	-0.0098
Final	-0.0989 (10)	-0.1034 (7)	-0.0097 (7)	-0.1034 (8)	-0.1041 (7)	-0.1035 (9)	-0.0098 (11)
ΔE(mV)	+4.6	-4.5	+93.8	-93.7	-0.6	+0.7	+93.8

it was found that in general, the e.m.f. differences thus obtained were less reproducible than those obtained from the final steady e.m.f. values. Hence for this electrode, the latter have been recorded in the table (ΔE). It will be seen that although electrode No. 28 had response characteristics similar to those of electrode No. 25, it appeared to be more erratic and less reproducible.

Following the procedure already adopted for the sodium responsive glass electrodes, the e.m.f. difference observed on transferring an electrode between two solutions, may be regarded as the e.m.f. of a concentration cell:

Ag-AgCl	KCl (m_1) Solution 1.	glass electrode	glass electrode	KCl (m_2) Solution 2.	AgCl-Ag

TABLE 10.15. (Cont.)

Electrode No. 25

6/9/66 (1) (Cont.)

Solution	Acetate 1.0m K^+ p_wH 4.81	0.1m Cl^-/E 1.0m K^+ p_wH 10.05	0.1m HCl 1.0m K^+ p_wH 1.29
Time(min.)			
0	-0.0988	-0.1034	-0.1067
1	-0.0988	-0.1034	-0.1066
2	-0.0989	-0.1035	-0.1066
5	-0.0989	-0.1035	-0.1066
Final	-0.0989 (9)	-0.1035 (9)	-0.1066 (8)
ΔE(mV)	+4.6	-93.7	-7.7

TABLE 10.15 (cont)

Electrode No. 25 (GKN 33) 6/9/66 (2)

Initial Solution
0.1m HCl, 1.0m K^+, p_wH 1.29

Final e.m.f. -0.1067
(Constant - 10 min.)

Solution	Acetate 1.0m K^+ p_wH 4.81	0.1mCl^-/E 1.0m K^+ p_wH 10.05	0.1m HCl 1.0m K^+ p_wH 1.29	0.1mCl^-/E 1.0m K^+ p_wH 10.05	0.1mCl^-/E 0.1m K^+ p_wH 9.95	0.1mCl^-/E 1.0m K^+ p_wH 10.05	Acetate 1.0m K^+ p_wH 4.81
Time (min)							
0	-0.0989	-0.1034	-0.1067	-0.1033	-0.0097	-0.1034	-0.0989
1	-0.0989	-0.1034	-0.1066	-0.1034	-0.0097	-0.1034	-0.0989
2	-0.0989	-0.1034	-0.1066	-0.1034	-0.0098	-0.1035	-0.0989
5	-0.0990	-0.1035	-0.1067	-0.1035	-0.0098	-0.1035	-0.0989
Final	-0.0990 (9)	-0.1035 (8)	-0.1067 (10)	-0.1035 (9)	-0.0098 (8)	-0.1035 (12)	-0.0989 (8)
ΔE (mV)	+7.8	-4.4	-3.1	+3.3	+93.7	-93.6	+4.6

TABLE 10.16.

Electrode No. 28 (GKN 33) 6/9/66 (1)

Initial Solution

$0.1mCl^-/T$, $1.0mK^+$, p_wH 9.13

Final e.m.f. -0.1018

(0.1mV decrease in 9 min)

Solution	$0.1mCl^-/E$ $1.0m\ K^+$ p_wH 10.05	$0.1mCl^-/E$ $0.1m\ K^+$ p_wH 9.95	$0.1mCl^-/E$ $1.0m\ K^+$ p_wH 10.05	$0.1mCl^-/T$ $1.0m\ K^+$ p_wH 9.13	Acetate $1.0m\ K^+$ p_wH 4.81	$0.1mCl^-/E$ $1.0m\ K^+$ p_wH 10.05	$0.1mCl^-/E$ $0.1m\ K^+$ p_wH 9.95
Time (min)							
0	-0.1010	-0.0075	-0.1010	-0.1017	-0.0987	-0.1018	-0.0079
1	-0.1009	-0.0075	-0.1010	-0.1019	-0.0986	-0.1015	-0.0078
2	-0.1009	-0.0076	-0.1010	-0.1020	-0.0985	-0.1014	-0.0079
5	-0.1009	-0.0076	-0.1010	-0.1021	-0.0983	-0.1013	-0.0079
10		-0.0077			-0.0981	-0.1013	-0.0079
Final	-0.1009 (8)	-0.0077 (10)	-0.1010 (8)	-0.1021 (9)	-0.0981 (13)	-0.1013 (15)	-0.0079 (12)
ΔE(mV)	+0.9	+93.2	-93.3	-1.1	+4.0	-3.2	+93.4

The e.m.f. values observed with the glass electrodes were compared, as before, with values calculated using activity coefficient data for unbuffered KCl solutions, having the same ionic strengths as the buffered solutions used here. The 1.0m KCl buffered with ethanolamine was chosen as the reference solution (solution 1 in the above cell) since the response of the electrodes to changes of potassium ion concentration, were investigated with solutions containing this buffer. The activity coefficient data of Robinson and Stokes[55] were used and the theoretical e.m.f. values thus obtained are given in table 10.17. The concentration cell e.m.f. values actually observed with the two glass electrodes, are given in table 10.18, and any difference between the observed and calculated values has again been regarded as due to a glass electrode error in solution 2.

6/9/66 (Cont)

TABLE 10.16 (Cont)

Electrode No. 28

Solution	0.1m Cl^-/E 1.0m K^+ P_wH 10.05	0.1m HCl 1.0m K^+ P_wH 1.29
Time (min)		
0	-0.1012	-0.1109
1	-0.1013	-0.1105
2	-0.1013	-0.1103
5	-0.1012	-0.1102
10		-0.1103
Final	-0.1012 (8)	-0.1103 (13)
ΔE(mV)	-93.4	-9.0

TABLE 10.16 (Cont)

Electrode No. 28 (GKN 33) 6/9/66 (2) Initial Solution

0.1m HCl, 1.0m K^+, p_wH 1.29

Final e.m.f. -0.1104

(constant - 8 min.)

Solution	0.1mCl^-/E 1.0m K^+ p_wH 10.05	Acetate 1.0m K^+ p_wH 4.81	0.1mCl^-/E 1.0m K^+ p_wH 10.05	0.1mCl^-/T 1.0m K^+ p_wH 9.13	0.1mCl^-/E 1.0m K^+ p_wH 10.05	Acetate 1.0m K^+ p_wH 4.81
0	-0.1009	-0.0979	-0.1011	-0.1022	-0.1014	-0.0974
1	-0.1014	-0.0979	-0.1014	-0.1023	-0.1015	-0.0976
2	-0.1016	-0.0980	-0.1015	-0.1023	-0.1015	-0.0978
5	-0.1016	-0.0980	-0.1015	-0.1024	-0.1015	-0.0983
10	-0.1016		-0.1015	-0.1025		-0.0985
Final	-0.1016 (10)	-0.0981 (9)	-0.1015 (11)	-0.1025 (16)	-0.1015 (9)	-0.0985 (24)
ΔE(mV)	+8.8	+3.6	-3.4	-1.0	+1.0	+3.0

TABLE 10.17.

Calculated E.m.f. values for KCl Concentration Cells

Solution 1. $0.1m Cl^-$/Ethanolamine + 1.0m KCl

Solution 2.	Ionic Strength	Molal Activity Coefficient	Calculated E.m.f.(mV)
a) $0.1m Cl^-$/Ethanolamine + 1.0m KCl $0.1m Cl^-$/Tris + 1.0m KCl 0.1m HCl + 1.0m KCl	1.1	0.598*	0.0
b) 0.1m Acetate + 0.9m KCl	1.0	0.604	+4.6
c) $0.1m Cl^-$/Ethanolamine + 0.1m KCl	0.2	0.718	+93.5

Calculated e.m.f. for the cell:-

Ag-AgCl	1.0m K^+ Acetate	glass electrode - glass electrode	1.0m K^+ 0.1m HCl	AgCl-Ag	

- 4.6 mV

* Value obtained by graphical interpolation.

TABLE 10.18.

Observed E.M.f. Values for KCl Concentration Cells (mV).

a) Solution 1. 0.1m Cl^-/Ethanolamine + 1.0m KCl, p_wH 10.05.

Solution 2.			Electrode No.25		Electrode No.28	
Buffer	p_wH	m_{K^+}	E.m.f.	Error	E.m.f.	Error
0.1m Cl^-/Tris.	9.13	1.0	-0.6	+0.6	-0.9	+0.9
			-0.7	+0.7	-1.1	+1.1
					-1.0	+1.0
					-1.0	+1.0
Acetate	4.81	1.0	+4.6	0.0	+3.2	+1.3
			+4.5	+0.1	+3.6	+1.0
			+4.6	0.0	+3.4	+1.2
			+4.4	+0.2	+3.0	+1.6
			+4.6	0.0		
0.1m Cl^- Ethanolamine	9.95	0.1	+93.8	-0.3	+93.2	+0.3
			+93.7	-0.2	+93.3	+0.2
			+93.8	-0.3	+93.4	+0.1
			+93.7	-0.2	+93.4	+0.1
			+93.7	-0.2		
			+93.6	-0.1		
0.1m HCl	1.29	1.0	-3.1	+3.1	-9.0	+9.0
			-3.3	+3.3.	-8.8	+8.8

b) Solution 1. 0.1 Acetate + 0.9m KCl, p_wH 4.81.

Solution 2			Electrode No.25	
Buffer	p_wH	m_{K^+}	E.m.f.	Error
0.1m HCl	1.29	1.0	-7.7	+3.1
			-7.8	+3.2

Before discussing the extent of the agreement between the observed and calculated values, the reproducibility of the values shown by the glass electrodes will be considered. Leaving aside for the present the data for the 1.0m KCl in hydrochloric acid, since it is probable that the hydrogen ion interferes with the cation response at this low pH, it is seen that the agreement between the two glass electrodes is not as good as was observed during the corresponding experiments with the sodium responsive electrodes. However, except for transfers of electrode No. 28 to and from the solution buffered with acetate, the e.m.f. differences shown by each individual electrode were reproducible to ±0.1mV.

On comparing the observed and calculated values, it is seen that electrode No. 25 agreed well with the calculated values for the acetate, and ethanolamine + 0.1m KCl solutions, but showed errors in the tris buffer and the potassium chloride solution in hydrochloric acid. Electrode No. 28, on the other hand, only agreed with the calculated value for transfers between the two ethanolamine buffers with different potassium chloride concentrations and it showed larger errors than electrode No. 25 for transfers to any of the other solutions. The errors observed with both electrodes for transfers between the 1.0m KCl buffered with ethanolamine and tris are somewhat surprising but it is possible that these electrodes show some response to the cations of the organic bases, particularly as they are known to respond to ammonium ions. It was noted above that electrode No. 25 showed good agreement with the theoretical e.m.f. difference when transferred between the 1.0m

potassium solutions buffered with acetate and ethanolamine. Hence if the acetate buffer with added potassium chloride is used as a second reference solution for this electrode, consistent results will be obtained. It can be seen from table 10.18 that this procedure was used to present some of the data for the solution of potassium chloride in hydrochloric acid.

The errors observed for both electrodes at low pH were almost certainly due to interference by the hydrogen ion as was also believed to be the case for the sodium responsive electrodes. However the time dependence of the e.m.f's. observed for the potassium responsive electrodes in the 1.0m KCl at p_wH 1.29, showed a marked contrast to the large transients observed with the sodium responsive electrodes, during the corresponding experiments, involving sodium solutions of about the same pH. With electrode No. 25 for example, both after transfer to the potassium chloride solution in hydrochloric acid, and after transfer back to a potassium solution of higher pH, the observed e.m.f. was almost constant (Response E). On the other hand, during a similar experiment with electrode No. 28, small transients were observed. However, with this electrode the observation of transients was not peculior to experiments with the potassium chloride solution containing hydrochloric acid, since other transients, which were at least as large, were sometimes observed after transfers between pairs of solutions of higher pH.

On account of the speed with which these potassium sensitive electrodes attained a steady e.m.f. in the solution of low pH, there was time to test electrode No. 25 in the solution twice. It may be seen from table 10.18 that

the errors shown by the glass electrode during the two experiments were in very good agreement. However there was considerable difference in the magnitudes of the errors shown by the two glass electrodes, and since electrode No. 28 gave a rather larger error than electrode No. 25, it seems possible that the error observed for electrode No. 28 in the acetate buffer was also due to the hydrogen ion.

Considering the erratic behaviour of electrode No. 28, it seems possible that this was a poor specimen and that the data for electrode No. 25 are therefore more typical. It would have been desirable had time permitted, to test more electrodes of this type, however the discrepancies discussed above can really only be resolved by experiments in which the glass electrodes are compared with potassium amalgam electrodes.

CHAPTER 11.

Discussion 1. - Glass Electrode Performance

The results obtained in this investigation may be examined in two ways. First one may consider what information they provide concerning the response characteristics of glass electrodes and second whether they throw any light upon the means by which glass electrodes function and the various theories that have been put forward. The first aspect of the data will be considered here and the second will be dealt with in the final chapter. The results of the present work will therefore now be compared with those of previous investigations and recommendations will be made concerning the experimental procedures which should be used in order to make precise pH, pNa or pK measurements with glass electrodes. Suggestions for further experiments will also be made.

11.1. pH Responsive Electrodes with Lithia Glass Membranes.

The errors shown by a lithia glass electrode in alkaline solutions containing lithium ions were in general never smaller than the errors for the corresponding sodium solutions and this was in agreement with the observations of Ssokolov and Passinski[5]. For the Radiometer B, Jena HA and Corning electrodes, the lithium error was much larger than the sodium error at a given pH, and only the Pye Ingold and Radiometer C electrodes (the second group of pH responsive electrodes) showed lithium and sodium errors of about

the same magnitude. For the latter electrodes the errors first appeared below pH 11, that is lower than the minimum pH stated by Ssokolov and Passinski but it must be remembered that these workers used lithium hydroxide solutions and hence the lithium ion concentration was not constant but increased with increasing pH. Hence the statement that lithia glass electrodes show large alkaline errors in lithium solutions, which has been made in several monographs, has been shown to be correct. However, in view of the fact that three unsuccessful attempts were made to repeat the original work of Ssokolov and Passinski, this statement has, until now, hardly been justified.

The results obtained in the present work may also be compared with those of Simon and Wegmann[72,73] who used electrodes made from the same glasses as some of the commercial electrodes tested here. In Chapter 2 (page 20) it was noted that Simon and Wegmann observed the time variations of the errors shown by their electrodes and designated them to one of six possible types. These types of response can be correlated with the classification used in the present work as follows:-

This work		Simon and Wegmann
C_1	A	Type C has an approximately constant
	C	final e.m.f.
D_1	B	Type D has an approximately constant
	D	final e.m.f.
C_2	F	
D_2	E	

It is possible, therefore, to compare the types of response observed for alkaline sodium solutions in the two investigations for those types of electrode which were common to both. A similar comparison of the magnitudes of the errors or of the e.m.f.-time variations could not be made, since the solutions used in the two investigations were not the same. The results of the present work have indicated that the type of e.m.f.-time variation observed when testing a glass electrode may depend upon the nature of the cation in solution but is apparently independent of the cation concentration or the pH.

The e.m.f.-time variations observed in the two investigations have been compared in table 11.1. The table includes data for both soda and lithia glass electrodes but discussion of those for the soda glass electrodes will be postponed until the next section. For most of the types of lithia glass electrode listed the same type of response was observed in both investigations. The only exception was the Beckman type E2 which in the present work always gave type D_1 response, like the majority of the lithia glass electrodes, but which Simon and Wegmann observed to give C response. The explanation for this is not clear but it is possible that the manufacturer has made some change in the glass composition since Simon and Wegmann carried out their work.

Simon and Wegmann also tested the response of their electrodes in the intermediate pH range but the precision of their experiments was not as high as those of the present work. In this investigation, even the less precise glass electrodes have been shown to agree with the hydrogen electrode to

TABLE 11.1.

Types of Response observed in this Investigation and by Simon and Wegmann for glass electrodes in alkaline sodium solutions

Type of Electrode	Response. This Work.	Response. Simon and Wegmann	
Beckman E2.	D_1	AF	(C_1 and C_2)
E.I.L. GHS 33	D_1	D	(D_1)
Jena HA	D_1	D	(D_1)
Corning 015 (E.I.L. GG 33)	C_1 D_2 D_1	A	(C_1)
Jena H	C_1 D_1	C	(C_1)

Simon and Wegmann used a double symbol A.F to indicate that either the two types of e.m.f-time variation were observed in two different experiments or that the e.m.f-time variations observed could not be unambiguously assigned to either type.

In the right hand column are given the designations used by Simon and Wegmann together with the corresponding symbol for the classification used in the present investigation in brackets.

$\pm$0.5mV over the pH range from about 0 (1.0m H_2SO_4) to 10 (ethanolamine buffer). This is a precision of 591.6 $\pm$ 0.5mV over 10pH units or 59.16 $\pm$ 0.05mV per pH unit, which is rather more accurate than the data of Simon and Wegmann who observed a range of 58.6 to 59.4mV per pH unit for their various electrodes. The best electrodes tested in the present work showed a response of 59.16 $\pm$ 0.02mV per pH unit over this range and the Radiometer B and Jena HA electrodes agreed with the hydrogen electrode to $\pm$0.2mV up to pH 13 when they were tested in the tetra-alkylammoniom hydroxide solution.

It might be helpful to point out here, that to express the precision of response in terms of mV per pH unit may be misleading. For example it has been stated above that in the present work, a good electrode showed a response of 59.16 $\pm$ 0.02mV per pH unit. This tends to imply that the electrodes agreed with the hydrogen electrode to $\pm$0.02mV when they were transferred between two solutions whose pH differed by only one unit. This of course was not the case. The experimental precision was $\pm$0.2mV in all transfers irrespective of the magnitude of the pH difference between the two solutions.

For several types of glass electrode tested in this work the magnitudes of the errors may also be compared with data supplied by the manufacturers. This data refers to the practical pH scale whereas the p_wH scale has been used in the present work. It was pointed out in section 5.4, that on the practical scale an unknown pH (pH_x) is measured in terms of the pH value assigned to a standard buffer (pH_s), and the e.m.f's. of the following cells:

$$(Pt)\ H_2\ (1\ atm.) \mid \text{solution } pH_s \mid \text{Sat.KCl} \mid Hg_2Cl_2 - Hg \qquad (E_s)$$

$$(Pt)\ H_2\ (1\ atm.) \mid \text{solution } pH_x \mid \text{Sat.KCl} \mid Hg_2Cl_2 - Hg \qquad (E_x)$$

The unknown pH is calculated from the relation

$$pH_x = pH_s + \frac{F(E_x - E_s)}{2.303RT}$$

and the value obtained in this way using cells with hydrogen electrodes was referred to as the 'correct pH'.

In practice the hydrogen electrode is replaced by a glass electrode and in the intermediate pH range the e.m.f. difference $(E_x - E_s)$ observed with a glass electrode, is in close agreement with that shown by the hydrogen electrode. As has been seen, the precision actually attained will depend upon the type of glass electrode used. In alkaline solutions containing small inorganic cations, however, all glass electrodes show positive errors and hence the observed e.m.f. difference, and consequently also pH_x, will be lower than the correct values. To enable those making pH measurements of alkaline solutions to allow for these errors, some of the electrode manufacturers supply data in the form of nomographs. This data is usually limited to solutions containing sodium ions since these are encountered more frequently than solutions of the other alkali metal cations. For the convenience of the electrode user the errors are presented in the form of correction factors to be added to the apparent pH_x values observed on a pH meter for given sodium ion concentrations.

Hence in order to compare the magnitudes of the errors stated by the

manufacturers with those observed in the present work it is necessary to know the corresponding apparent pH values shown by the glass electrode on the practical scale. The relationship between the practical pH scale and the p_wH scale used in this work was considered in section 5.4, and a method of estimating the correct pH on the practical scale from the measured p_wH was explained. Essentially this procedure involved the estimation of the pH of the solution defined as - log a_{H^+}, taking the activity coefficient of the chloride or bromide ion to be equal to the mean ionic activity coefficient of the appropriate electrolyte; and the value obtained was regarded as being equal to the correct pH on the practical scale. It was shown that for all the 1.0m sodium solutions used in this work, the correct pH on the practical scale could be estimated from the p_wH by the equation:

$$pH_x = p_wH - 0.18$$

If the error of the glass electrode is ΔpH then the corresponding apparent value of pH_x is given by:

$$pH_x \text{ (apparent)} = p_wH - 0.18 - \Delta pH$$

The argument used to obtain the equation relating the p_wH and the correct pH on the practical scale, contained three assumptions; first that the pH value assigned to the standard buffer (pH_s), was equal to the negative logarithm of the hydrogen ion activity in that solution, second that the liquid junction potentials in the two cells were the same, and finally that the activity coefficient of the chloride or bromide ion was equal to the mean ionic activity coefficient of the appropriate salt. These assumptions may

have resulted in the calculated apparent pH_x being slightly different to the value that would have been observed if this quantity had actually been measured on a pH meter. However since the error shown by a glass electrode in solutions of a given cation content, increases relatively slowly with increase of pH, it is possible, even if the estimated apparent pH_x values are accurate to no better than 0.1 of a pH unit, to read the errors from the manufacturers' nomographs to the nearest 0.01 of a pH unit. This is sufficiently accurate for comparison with the present work.

No information is supplied with the E.I.L. GHS 33 or Pye Ingold electrodes and that given for the Jena HA electrodes did not include a sodium concentration of 1 molal. The nomograph supplied by Radiometer is limited to 20°C and hence the errors estimated from it might be expected to be a little lower than those observed in this work. Only the data supplied with the Corning and Beckman E2 electrodes covered a range of temperatures and included 25°C.

Since the manufacturers' data make no reference to the time dependence of the errors they presumably refer to those parts of the e.m.f.-time curves where the errors become approximately constant. The errors predicted by the manufacturers' nomographs have therefore been compared with the final errors observed in this work and details are given in table 11.2. for those types of electrode where such a comparison is possible. The electrodes often gave transients after transfer to alkaline sodium solutions; however the variation in the apparent pH_x due to one of these transients would have almost negligible effect upon the value of the error indicated by the nomograph.

TABLE 11.2.

Comparison of Errors with Manufacturers' Data

Beckman E2 Electrodes

p_wH	Electrode	Test	Observed Error		Apparent pH_x	Predicted Error
			mV	pH		pH
13.00	3	73	+3.1	-0.05	12.8	-0.08
	19	74	+2.6	-0.04	12.8	-0.08
11.97	3	72	+1.5	-0.025		
	19	20	+1.4	-0.02	11.8	-0.025
	19	21	+1.6	-0.03		

Corning Electrodes

p_wH	Electrode	Test	Observed Error		Apparent pH_x	Predicted Error
			mV	pH		pH
13.00	27	41	+3.3	-0.06		
	27	42, 44, 45 (Average)	+2.3	-0.04	12.8	-0.01
	30	43	+1.8	-0.03		

TABLE 11.2. (Cont.)

Radiometer B Electrodes

p_wH	Electrode	Test	Observed Error		Apparent pH_x	Predicted Error (20°C)
			mV	pH		pH
13.00	4	13	+3.4	-0.06	12.8	-0.06
	17	2,7,26,27 (Average)	+4.5 ±0.5	-0.075 ±0.005	12.7	-0.06
11.97	4	12	+1.6	-0.03	11.8	-0.02
	17	6, 8 (Average)	+1.4	-0.02	11.8	-0.02

Radiometer C Electrodes

p_wH	Electrode	Test	Observed Error		Apparent pH_x	Predicted Error (20°C)
			mV	pH		pH
9.85	7	61,62	+2.6	-0.04	9.6	-0.035
	16	59	+3.0	-0.05	9.6	-0.035
10.5	7 and 16	9,60,63 (Average)	+5.4 ±0.4	-0.10	10.2	-0.06
10.55	16	56	+7.1	-0.12	10.25	-0.06
11.97	16	10	+22.1	-0.37	11.4	-0.20
		11	+22.6	-0.38	11.4	-0.20

When considering the data in table 11.2, it is important to remember that the manufacturers' correction factors are intended for distribution with the large numbers of electrodes offered for sale. There are usually small differences in performance even between electrodes with membranes made from the same glass melt, and the magnitudes of the errors shown by individual electrodes at any given time will probably depend upon the nature and extent of their previous useage. Hence the errors indicated by the manufacturers' nomographs can only be approximate or average values. In the present work the reproducibility of the errors observed for a given alkaline solution during duplicate experiments with the same electrode, or electrodes of the same type, was about ±0.01 of a pH unit, and although it would have been desirable to investigate the reproducibility of the errors further, the data obtained are probably fairly representative of each type of electrode tested.

For the group 1 electrodes listed in table 11.2, the agreement between the observed final errors and those predicted by the manufacturers' data was particularly good for p_wH 11.97. However for p_wH 13.00, the errors indicated by the manufacturers' nomographs in some cases differed from the observed values by amounts which were outside the level of reproducibility observed in this work. The largest deviation was observed in test 41 for the Corning electrode No. 27, but the electrode gave an exceptionally large error in this experiment which as suggested in section 7.2, may have resulted from testing it in lithium solution earlier on the same day. Nevertheless even leaving aside this experiment, the differences were between 0.02 and 0.04 of a pH unit.

A difference of 0.02 of a pH unit is probably acceptable since a more extensive investigation involving a larger number of electrodes, might reveal that the reproducibility of the alkaline errors between different electrodes of the same type, is not as good as the ±0.01 of a pH unit observed here. However for pH 13 the error predicted by the Corning nomograph is certainly too low, whereas that given for the Beckman electrodes is too high. The errors obtained from the Radiometer nomograph for their type B electrodes were in fair agreement with the observed values. However the predicted values for their type C electrodes (classified in this work as group 2) were all lower than the errors observed with either of the electrodes tested, and are probably too low for the discrepancies to be accounted for by the temperature difference. Hence, even allowing for the inevitable limitations of the manufacturers' data, there are several instances where the stated and observed errors were in poor agreement.

The manufacturers' leaflets and literature, except that of Radiometer, also make mention of the relative magnitudes of the errors observed in the presence of different cations, but this is only qualitative and no data is given. The Corning and Beckman leaflets state that the errors due to ions other than sodium are smaller than those at the corresponding sodium concentration, but on the other hand in the Jena pamphlet No. 2220e, it is said that the alkaline error increases in the sequence $K^+ < Na^+ < Li^+$. It has been shown in this work that some lithia glass electrodes including the Jena HA and Corning, give larger errors in lithium solutions than in sodium

solutions of the same concentration and pH. Hence the Corning leaflet is undoubtedly incorrect in this respect. The Beckman leaflet is probably also wrong on this point, but since Beckman electrodes have not been tested in lithium solutions this has not been established with certainty.

As was mentioned earlier, some of the results of the present work appear to indicate that the alkaline errors of individual electrodes might have a reproducibility of ±0.01 of a pH unit or better under suitable conditions. In order to confirm this, however, a more extensive investigation would be necessary with several electrodes of a given type end more tests of each than has been possible here in this general survey of glass electrode performance. Nevertheless even if it could be established that the above precision is attainable, the manufacturers' data cannot be other then the average errors shown by their electrodes. However it would then be possible for glass electrode users to determine correction factors for the alkaline errors, accurate to ±0.01 of a pH unit, for their own particular electrodes.

In order to attain this level of reproducibility, an electrode would probably not have to be used in solutions likely to produce a change in the surface of the glass membrane. Acid solutions containing fluoride ions would obviously be avoided and it would probably also be advisable not to use the electrode in alkaline lithium solutions since it has been observed that these may cause considereble changes in asymmetry potential with some electrodes. There is some evidence that the errors increase as an electrode becomes older and hence they may not remain reproducible over periods of more than a few weeks.

A question which is important for glass electrode users is how to select from among the alternatives commercially available, the type of electrode best suited to the purpose in hand. For example it may be required to use a glass electrode in place of hydrogen electrodes in order to make e.m.f. measurements accurate to ±0.2mV or better in solutions of intermediate pH. In this pH range all the available glass electrodes are uninfluenced by any ions in the solution other than the hydrogen ion and it has been found that the Radiometer Band C, Jena HA and Corning are preferable to the Beckman E2, Pye Ingold and E.I.L. GHS 33 electrodes for this purpose. If on the other hand it is proposed to make pH measurements in alkaline solutions, the first factor to be considered is the relative magnitudes of the errors shown by the different types of electrode in solutions of various cations. The electrode which shows the smallest errors in solutions of a particular cation content can be used up to the highest pH before the errors appear.

It has been found in the present work that the electrodes which show the smallest errors in alkaline solutions in general, show much larger errors in lithium solutions than in sodium solutions. Hence if possible it is desirable to avoid the use of lithium solutions and if the alkali metal cation can be replaced by a tetra-alkylammonium ion then no errors will be observed even at high pH. However, if it is necessary to use solutions where all the available electrodes show errors, then the electrode with the smallest error will not necessarily be the best, since if correction factors are to be applied, the reproducibility of the error now becomes important. Since it is

probably true that the smaller the error the better the reproducibility, the electrodes showing the smallest errors are likely to be the most satisfactory in this respect also. An additional advantage to the average user will be that when the error is small the time taken to attain an approximately constant e.m.f. is usually small also.

Of the four types of electrode selected above as having the most precise pH response in the intermediate range, the Corning showed the smallest errors in alkaline solutions containing sodium ions. In fact they showed smaller errors than any other type of electrode tested. For lithium solutions however, an electrode of this type showed large non-reproducible errors accompanied by changes of asymmetry potential and for these solutions the Jena HA or Radiometer B electrodes are certainly superior. It should perhaps be pointed out that it was not possible in this work to test the reproducibility of the sodium errors of the Corning electrodes over a period of weeks or months, and they may increase as the electrodes become older. When an electrode of one of the three types just mentioned is used in an alkaline solution containing sodium ions or when a Radiometer B or Jena HA electrode is used in alkaline lithium solution the final steady e.m.f. is the one which shows least error.

11.2. pH Responsive Electrodes with Soda Glass Membranes

It has already been pointed out that experiments with pH Responsive

soda glass electrodes are nowadays of more academic than practical interest since for most practical purposes these electrodes have replaced those having lithia glasses. In this investigation a phenomenon has been observed which demonstrates the influence of pre-treatment on the response of soda glass electrodes and if investigated further this might ultimately contribute to a better understanding of the means by which glass electrodes function. Before suggesting further experiments however, the results obtained in the present work will be compared with those of previous investigations.

The most extensive previous investigation of the alkaline errors of soda glass electrodes was that carried out by Dole[11,12]. However unlike Simon and Wegmann[72,73] who also tested some soda glass electrodes, Dole did not follow the time dependence of the errors shown by his electrodes. The types of e.m.f.-time variation observed by Simon and Wegmann in their work were listed in the last section and their results for soda glass electrodes were given in table 11.1. In the present investigation the type of response shown by the soda glass electrodes seemed to depend rather more on the individual electrode than was the case for the electrodes having lithia glass membranes. Nevertheless the type C_1 response which was observed by Simon and Wegmann was also shown by several soda glass electrodes tested in the present work.

Dole recorded only the final approximately constant errors shown by his electrodes. However in the present work where the time dependence of the errors has been considered, it has been found that this final error is the

one most suitable for comparison of different experiments. On this basis Dole observed that the relative magnitudes of the errors for solutions containing different alkali metal cations was $Na^+ > Li^+ > K^+$ and this was confirmed in the present work. Dole presented his results as the average error shown by several electrodes in each solution. He found that the values obtained during different investigations did not always agree and suggested that this was due to small differences in glass composition. While this explanation is possible the discrepancies were probably at least partly due to the shortcomings of Dole's experimental technique discussed in chapter 5. Also the results of the present work have demonstrated the influence of the pretreatment of soda glass electrodes upon their alkaline errors, a factor of which Dole and other previous workers were almost certainly not aware.

It has frequently been stated that in solutions which do not contain small inorganic cations, soda glass electrodes are error-free up to a pH of about 11. However this is largely based upon the early work of Hill[27] using ammonia buffers, when the precision was only ±0.01 of a pH unit. In the present work it has been shown that in solutions which contain only large organic cations, soda glass electrodes do in fact agree with the hydrogen electrode to ±0.2mV and often better up to p_wH 10.5. Several previous workers have reported that at high pH soda glass electrodes show much smaller errors in the tetra-alkylammonium hydroxides than in solutions of the inorganic hydroxides. This has been confirmed in the present work and it has been suggested that these small errors which have been observed in the tetra-alkylammonium hydroxide solutions are really due to inorganic cations present as impurities.

It has also been found in the present investigation that the errors of soda glass electrodes in acid solutions are less reproducible than the alkaline errors. This is further borne out by comparison of the results obtained here with those of Caudle[1] for electrodes of the same types; E.I.L. GG 33 and Jena H. However although the acid errors of soda glass electrodes are not very reproducible it seems unlikely that the irreproducibility can account for the incorrect results obtained by the early workers in this field. For example, MacInnes and Belcher's incorrect conclusion that the acid errors increase in the order

$$HCl < H_2SO_4 < H_3PO_4$$

was presumably a result of either faulty measuring equipment or unsatisfactory electrodes, since the errors observed for these acids are now known to be in the reverse order and the difference in magnitude is fairly large. In 5m HCl the error is about 100mV whereas in 5m sulphuric or phosphoric acids it is small or zero. Experiments with concentrated magnesium sulphate solutions in this work did not confirm the so-called water activity errors reported by Amis and Gabbard[15] and again one must conclude that either the electrodes or the measuring circuit used in the earlier work were not satisfactory. In fact Perley[8] suggested that the thin membrane type of electrode used in many of the early investigations was unreliable "as glass stability may be an important characteristic".

The increase in the alkaline errors of soda glass electrodes produced by treatment with acid solution, which has been observed in the present work was

apparently also noticed by Dole, Roberts and Holley[16] in 1941. However these workers only observed the effect for hydrofluoric acid, a 0.98N potassium fluoride solution in an acetate buffer of pH 4.14, and did not realise that it could also be produced by other acids. They recorded a negative error of 123mV for a soda glass electrode in the above solution and then added 1N potassium hydroxide solution to bring the pH up to 12.25 when a positive error of 69mV was noted. The error in this solution, shown by a similar electrode which had never been in a fluoride solution of pH less than 6.34, was only 49mV. Two observations might be made concerning this experiment. Firstly a solution of this fluoride concentration and pH would probably have attacked their cell vessel but this possibility was apparently not considered. Secondly it is possible that a large error of 123mV represents considerable attack of the glass surface by the fluoride solution and the electrode may have been no longer showing the 59mV per pH unit response even between solutions where acid and alkaline errors were not observed. It is unfortunate that they did not test the electrode in a few solutions of intermediate pH before determining the error at pH 12.25.

This effect produced by HCl and other acids on the alkaline errors of soda glass electrodes, which has been observed in this work, seems worthy of further investigation. Experiments with radioactive tracers, for example, might yield information which would contribute not only to an understanding of this phenomenon but perhaps ultimately towards a complete understanding of the functioning of the glass electrode. Using this technique it might be possible

to determine whether any anion from the acid is retained in the electrode surface when it is tested in the alkaline solution, and also whether the adsorption by the glass electrode, of cations from the alkaline solution, increases after the electrode has been treated with acid. Alternatively the effect could be further investigated using the same techniques as in the present work. One might examine the dependence of the increase in alkaline error upon the following factors.

1. the pH and cation content of the alkaline solution and related to this the magnitude of the error observed under normal circumstances
2. the magnitude of the acid error
3. the time of immersion in the acid solution
4. the time between removing the electrode from the acid solution and testing it in the alkaline solution.

Each of these factors could be varied in turn while the others are kept constant. Of the two investigations just suggested that with radioactive tracers would probably be the most fruitful at this stage since the e.m.f. experiments would be time consuming and tedious and could not by themselves lead to any definite indication of the cause of this phenomenon.

11.3. Cation Responsive Electrodes

It is appropriate that the data obtained in the present work for electrodes responsive to cations other than the hydrogen ion should first of

all be compared with the observations of Mattock[40,41] since electrodes made from the same glasses were used in both investigations. As has been noted earlier, Mattock's work was concerned with the use of these electrodes for the measurement of cation concentrations rather than activities and his experimental procedure was chosen accordingly. The precision of his data was not as good as that of the present investigation. Mattock reported that although the response of the electrodes to change of cation concentration was linear, it was only about 95% of the theoretical value. By this he presumably meant that the response was about 56mV per pNa or pK unit. However, in the light of the present work where a response of 59mV per p_wNa or p_wK unit was observed, Mattock's observation was probably due to the experimental technique used rather than any failure of the electrodes. The response of the sodium sensitive electrodes was said to be linear over the pNa range 0 to 4 whereas for the potassium sensitive electrodes it was linear over the pK range 0 to 3. In the latter case Mattock suggested that the organic cation of the buffer interfered with the potassium response to a small extent.

Mattock pointed out the importance of the ratio of the hydrogen ion concentration in the solution to that of the cation, in determining whether there is any interference with the cation response by the hydrogen ion. For the BH 68 (GNA 33) glass it was stated[40] that if the ratio $\frac{C_{H^+}}{C_{Na^+}}$ is not greater than 10^{-3}, pH effects are negligible up to a pNa of 4 However, it was recorded that for a solution of pNa 4, a pH change from 10 to 7 brings about a change of 0.1 of a pNa unit (ie 6mV). For the BH 10% glass (GEA 33) the

corresponding maximum ratio was said[43] to be 10^{-4}. In the present investigation it has been found, in agreement with Mattock's observations, that the GNA 33 electrode showed a higher selectivity towards sodium ions than the GEA 33 electrodes since it gave smaller hydrogen ion errors at low pH. However, the pH values at which the errors first appeared for a given cation concentration, did not differ greatly between the two types of electrode. For precise work the maximum permissible $\frac{C_{H^+}}{C_{Na^+}}$ ratio is about 10^{-5} for both types of electrode since they gave small errors in 1 molal sodium solution at a p_wH of 4.75.

The selectivity of the GKN 33 electrode towards the potassium ion relative to the hydrogen ion has been found to be better than the selectivity of the sodium responsive electrodes towards the sodium ion. Mattock[41] stated that GKN 33 electrodes could be used in 0.001M potassium solution down to pH 6. In the present investigation one of the two GKN 33 electrodes gave no error in 1 molal potassium solution of pH 5 and the errors observed for both the electrodes in the 1.0m KCl + 0.1m HCl solution were smaller then those shown by the sodium responsive electrodes in the corresponding sodium solution. The maximum permissible $\frac{C_{H^+}}{C_{K^+}}$ ratio for precise work with these electrodes was therefore about 10^{-4}.

As was noted in chapter 3, Mattock investigated the speed of response of the electrodes to the appropriate cation in solutions buffered to a pH where the hydrogen ion does not interfere. He stated that the sodium responsive electrodes were not as fast as pH responsive electrodes and that the speed of response was dependent upon the sodium concentration of the solution and also

the size of the pNa transition. This was not found to be the case in the present work since at high pH the speed of response was comparable with that of the best pH responsive electrodes and the electrodes showed equally rapid response at each of the sodium concentrations investigated. It is true that the present work only covered the pNa range 0 to 2 but there is nevertheless reason to believe that the slower response observed by Mattock for solutions of high pNa values was due to interference by the hydrogen ion.

Mattock observed the speed of response of his electrodes using two solutions, each of pH 7, having slightly different sodium concentrations around 10^{-2}M (pNa = 2). He found that electrodes of the BH 104 glass required 2-3 minutes to achieve an e.m.f. steady to (0.01 pNa unit) 0.6mV, and the BH 68 electrodes required 4-5 minutes. In solutions of higher pNa longer times were required to achieve the same stability. If the observations for solutions of pNa 3 and 4 were also carried out at pH 7 - this is not clear in the paper - then the results of the present investigation show that sluggishness due to interference by the hydrogen ion would have occurred. The maximum permissible $\frac{a_{H^+}}{a_{Na^+}}$ ratio has been found to be 10^{-5} and when this was exceeded errors were observed accompanied by small but significant transients. Hence at pH 7 interference by the hydrogen ion would probably occur if the pNa value exceeds 2.

Furthermore the response reported by Mattock for solutions of pNa 2 was not as fast as that observed in the present work and this may have been due to the technique used by Mattock for transferring a glass electrode from

one solution to another. In fact, over the past few years, the procedure used when testing glass electrodes at the E.I.L. laboratories appears to have been changed. In 1960 when the GNA 33 electrode became commercially available, it was recommended[42] that before an electrode is placed in a new solution it should be washed with water and then wiped dry. Later[40], Mattock pointed out that "the technique of electrode usage can affect the response time significantly" and stated that washing with water causes a marked decrease in the speed of response. The technique recommended was therefore intermediate washing with a sample of the new solution and/or gentle wiping with tissue. Experience obtained in this work and in Caudle's investigation has indicated that the best procedure is simply to wash an electrode with a sample of the new solution as this causes least disturbance to the surface. Wiping the electrode surface is believed to produce spurious transients (feature A) which increase the response time.

In this context it is noteworthy that Mattock observed an increased speed of response for the GKN 33 (BH 115) potassium electrodes when a flow system was used instead of the transfer procedure. In 1962, he stated[82] that when one of these electrodes was washed and wiped with tissue before being placed in a new solution, it required about 2 minutes to achieve a reading constant to 0.01 - 0.02 of a pK unit. However later[41] using the flow technique he obtained a speed of response comparable with that found for pH electrodes, a reading to within 0.01pK unit of the final approximately steady value being reached in less than 30 seconds.

The difference in behaviour shown by the GNA 33 electrode used in this work and that used earlier by Covington is probably accounted for by the fact that the solutions in the earlier investigation had a p_wH of 4.4. In the present work the GNA 33 electrode gave an error and a large transient in a 1m sodium chloride solution at pH 2. One might expect to observe similar behaviour therefore in 0.1m NaCl at pH 3, in 0.01m NaCl at pH 4 and in 0.001m NaCl at pH 5. Hence the deviations from the predicted values and the sluggishness of response shown by Covington's electrode were almost certainly due to the occurrence of hydrogen ion errors in the solutions used.

Savage and Isard[47-49] also observed sluggish response of cation sensitive electrodes. These workers conditioned their electrodes in a 0.01N solution of the salt to be investigated and then made their e.m.f. measurements in the order of increasing alkali metal ion concentration beginning with a buffer solution without any added salt. However this procedure would almost certainly cause sluggish behaviour of the electrodes since it has been pointed out by Mattock that prolonged contact of a cation sensitive electrode with a very dilute solution will increase its response time. Reactivation can be achieved by soaking it in a more concentrated solution and Mattock suggested a 0.1m or 0.2m concentration of the appropriate cation for this purpose and also for electrode storage. Hence it seems probable that if Savage and Isard had tested their electrodes in the more concentrated solutions first, a much faster response might have been observed. It would perhaps also have been preferable to condition the electrodes in a more concentrated solution than

the 0.01N used. Savage and Isard also observed the influence of the technique of transferring an electrode to a new solution upon the speed of response. Before an electrode was placed in a new solution it was either washed with distilled water and wiped dry with filter paper or it was simply dried with filter paper to remove adhering solution. The latter procedure was preferred since washing with water was found to increase the drift of potential observed before the electrode attained its equilibrium value in the new solution. The response time would probably have been reduced if the electrodes had simply been washed with a sample of each new solution and then placed directly in the cell without any wiping.

Both Lanier[51] and Eisenman[39] have examined the response of sodium sensitive glass electrodes to changes of cation activity and the present work compares favourably with these investigations as far as reproducibility is concerned. In the present work the e.m.f. difference observed on repeated glass electrode transfers between a given pair of solutions was, almost without exception, reproducible to ±0.1mV provided the pH was high enough to prevent any interference by the hydrogen ion. This applied both to repeated testing of individual electrodes and from one electrode to another. The reproducibility of Lanier's work was in general ±0.2mV and Eisenman's data in some cases show a scatter of the order of 1mV. It is probable that had these workers made allowance for changes of the asymmetry potentials of their electrodes better reproducibility would have been obtained.

In the present work it has been shown that provided the pH is not too low

the response of these electrodes to changes of cation concentration is fast and reproducible, and hence further experiments to determine whether they show accurate response to the cation activity would be well worthwhile. It would be advisable to use solutions buffered to pH 8 or higher similar to those used in the present work since otherwise there will be interference by the hydrogen ion at the lower alkali metal cation concentrations, ie. about 10^{-3}m. The glass electrodes would be compared directly with amalgam electrodes and when transferred between two cells they would simply be washed with a sample of the new solution. In such an investigation it would be preferable to test a larger number of electrodes of each type than has been possible in the present work and also to introduce more different types of electrode.

In one respect the results obtained for cation sensitive electrodes have some bearing upon the mechanism of operation of pH responsive glass electrodes. It has been shown that cation sensitive electrodes are as fast in their response as the pH electrodes and hence a fast response is not a feature peculiar to the latter. It has previously been suggested that the fast response of pH sensitive glass electrodes was due to the uniqueness of the proton and electrodes showing a response to other cations were expected to be more sluggish.

One may also compare the time dependence of the e.m.f's. shown by the electrodes primarily sensitive to different cations including the hydrogen ion, in solutions where they gave errors. The potassium responsive electrodes showed virtually no time dependence of e.m.f. (Response E) in the solution of low pH where errors were observed. On the other hand the sodium responsive

electrodes showed transients in the corresponding sodium solutions which, relative to the size of the errors, were much larger than those in general observed for pH responsive electrodes in alkaline solutions. This is interesting in as much as it confirms Eisenman's observation than an electrode selective to the potassium ion "responds in a square manner to step changes of solution composition in mixtures of hydrogen and alkali metal cations". However it must be remembered that only one type of potassium responsive electrode was tested in this work and some makes of pH responsive electrodes also showed type E response in alkaline solutions whereas others gave transients.

CHAPTER 12.

Discussion 2 - Theories of Glass Electrode Performance

The theories which have been advanced to explain the operation of glass electrodes may be broadly divided into two types. The first type will be termed 'equilibrium theories', since they refer to the approximately constant final potential attained by a glass electrode in many solutions, whereas those of the second type are kinetic and concerned with the manner and rate with which this potential is attained. In the present work, much attention has been given to the time-dependence of glass electrode potentials and hence this discussion will deal mainly with the non-equilibrium theories. However the equilibrium theory which is now generally accepted, the so-called Phase Boundary Potential Theory, will be briefly reviewed since this theory has sometimes been used as a basis for a theoretical treatment of the approach to the steady state. All theories of the response of glass electrodes necessarily depend in part upon the available information about the structure of glasses and the state of a glass surface when exposed to aqueous solutions. The present state of knowledge in this respect will therefore be outlined before the theories are discussed.

12.1. The Structure of Glass and the Glass-Solution Interface

The investigation of glasses by X-ray techniques has provided confirmation for the structure originally proposed by Zachariasen[83]. In pure

silica, each silicon atom is linked to four oxygen atoms in tetrahedral configuration and each oxygen atom is linked to two silicon atoms. These tetrahedra form a continuous, random three dimensional network. The silicon dioxide is called a network former and the oxygen atoms are referred to as bridging oxygens. In silicate glasses containing an alkali metal or alkaline earth oxide, the metal cations are balanced by singly charged oxygen atoms each of which is attached to only one silicon atom. The cations fit into the interstices in the network adjacent to these so-called non-bridging oxygen atoms and the alkali or alkaline earth oxide is known as a network modifier. It has been known for some time that electrical conduction in glasses is ionic; for example, the experiments of Burt[84] in 1925 showed that the current is carried exclusively by the interstitial cations. The temperature dependence of the conductivity indicates that it is an activated process, a cation requiring a certain vibrational energy in order to cross the barrier between two interstitial sites.

Oxides of certain trivalent elements such as aluminium can be incorporated into the silica lattice and when one of these oxides is present in a glass it is referred to as the second glass forming oxide. In an aluminosilicate glass for example, provided there are sufficient alkali ions present to balance the negative charges, the aluminium forms AlO_2^- which is isoelectronic with SiO_2. The aluminium thus takes the place of silicon atoms in the lattice. The bonding of the alkali ions is now altered since the negative charges are no longer located on non-bridging oxygen atoms, and these glasses show a

selectivity for cations other than the hydrogen ion. The introduction of aluminium oxide into a glass also increases the electrical conductivity, again provided the alkali ion content is sufficiently high. This increase is thought to be due to the more open structure of the aluminosilicate network and probably accounts for the relatively low resistances of the cation sensitive electrodes used in this work.

It has been believed for some time that an essential requirement for the satisfactory functioning of a pH responsive glass electrode is the formation of a hydrated layer known as the 'gel layer' on the two surfaces of the glass membrane. As early as 1909, for example, Haber and Klemensiewicz[85] found that electrodes which normally showed the correct response gave irregular results if they were allowed to become dry and it is well known that for satisfactory results the membrane of a pH responsive glass electrode must be soaked in water for a period before use. It has also been shown by Hubbard and his collaborators[86], that there is a distinct correlation between the hygroscopicity of a glass and its electrode properties. Chemically resistant glasses of low hygroscopicity, such as are used in the manufacture of glass-ware, are unsuitable for the preparation of pH responsive electrodes. On the other hand, electrodes made from highly hygroscopic glasses such as Corning 015, show the correct pH response over a wide range. However it is apparently desirable that the hygroscopicity should not be too high, since although lithia glasses are known[87] to be less hygroscopic than those made from sodium oxide they nevertheless give the more satisfactory electrodes. Hence there may be an optimum hygroscopicity for a pH responsive electrode glass.

It is thought that this gel layer is formed by the exchange of alkali metal ions in the glass for hydrogen ions from the solution and this exchange is probably accompanied by the absorption of some water by the glass. Haugaard[88] investigated the interaction between 0.1M HCl and glass powder and found that the decrease in the acidity of the solution was equivalent chemically to the increase in "water of constitution of the glass". Hubbard, Hamilton and Finn[17] studied the attack of MacInnes-Dole glass by interferometry and found that, after treatment with aqueous solutions of intermediate pH, the glass became swollen. This ion-exchange phenomenon is also observed if a glass is placed in contact with a molten salt, and depending upon whether the exchanging cation is larger or smaller than the cation originally present, the glass either becomes swollen, or shrinks with the appearance of fine cracks on the surface.

Rana and Douglas[89] investigated the interaction between glasses and solutions by refluxing water over glass grains of various compositions. They found that initially attack of the glass occurred by a diffusion-controlled ion exchange mechanism with very little dissolution of the silica network. On prolonged exposure, the attack took place by a second mechanism which resulted in a much larger proportion of silica among the reaction products. The onset of this direct solution of the glass, thus prevented a thicker layer developing and their results indicated that the hydrated surface layer of a glass electrode is very thin, the bulk of the glass remaining unchanged even after prolonged use. Some reagents, notably hydrofluoric acid dissolve the

silica network so rapidly that no ion exchange takes place and the rate is not diffusion-controlled even in the earliest stages.

The potential at the surface of a glass electrode is believed to be established by the movement of ions between the solution and this gel layer. When a pH responsive glass electrode is in contact with standard solutions, the cations present in the gel layer are probably almost entirely hydrogen ions and the layer thus provides a medium of essentially constant hydrogen ion activity on the glass surface. Only hydrogen ions can cross the glass-solution interface and the potential is thus dependent only upon the pH of the solution. In acid and alkaline solutions where errors are observed, it is thought that ions other than hydrogen ions can participate in the electrode reaction and enter the gel layer. Before considering how this view has been treated quantitatively to obtain an equation for the glass electrode potential, possible qualitative explanations will be advanced for some of the observations made in the present work.

It has been demonstrated here that lithia glass electrodes show smaller errors in alkaline sodium solutions than do electrodes made from soda glass. This has been reported before, although the experimental evidence was rather doubtful, and the following explanation has been put forward by Perley[7]. Lithium ions having a low coordination number in the glass are strongly bound to the silicon-oxygen lattice and thus show little tendency to exchange with other larger cations, such as sodium ions, from the solution. However although this fact may well explain why lithia glasses are less hygroscopic than soda

glasses it does not seem a very plausible explanation of their lower alkaline errors.

As was indicated above, the alkaline errors of glass electrodes are believed to occur when cations other than the hydrogen ion enter the hydrated surface layer from which the original cations have been exchanged for hydrogen ions. It is probable therefore than an important factor will be the size of the holes in the silica network left by the original cations. The lithium ion is small, thus for a lithia glass these holes will be relatively small. Hence larger cations in the solution will be able to penetrate the gel layer less readily than for a soda glass electrode.

If the magnitudes of the alkaline errors were determined solely by these steric factors, one might expect all glass electrodes to show larger errors in lithium solutions than in the corresponding sodium solutions. However it is found that soda glass electrodes show smaller errors in lithium solutions than in sodium solutions of the same concentration and pH. Perley has suggested that the magnitudes of the alkaline errors are also determined by the ability of the alkali ions to associate with water. The lithium ion is strongly hydrated and therefore the size of the error shown by glass electrodes in alkaline lithium solutions may be largely determined by the ease with which the ion is removed from water.

The differences in response shown by the various electrodes when tested in dilute hydrofluoric acid solution may possibly be accounted for by differences in hygroscopicity. The soda glass electrodes showed response

similar to that observed for hydrochloric acid solutions in which they gave errors, whereas the lithia glass electrodes, with one exception, appeared to be subjected to much more drastic attack resulting in the temporary loss of pH response. This might be explained by the fact that soda glass electrodes have gel layers which contain more water and are probably thicker. Hydrofluoric acid attacks the silica network of a glass and this thicker gel layer may serve as protection and prevent the acid reaching the bulk of the glass. In the case of a lithia glass electrode the thinner gel layer appears to be rapidly dissolved away leaving the unchanged bulk glass open to direct attack by the hydrofluoric acid.

Finally the effect of the halogen acids upon soda glass electrodes and their response in alkaline solutions will be considered. As was stated in chapter 9, when these electrodes were tested in alkaline solutions after treatment with one of these acids, they gave large transients of type C_2 or D_1 irrespective of the type of response normally observed for these solutions. When C_2 response was observed, the initial increase in error was usually small compared with the decrease which followed, and hence the latter was quite the most prominent feature of the e.m.f-time variation. Thus the response now shown by these electrodes was much the same as that normally shown by the lithia glass electrodes in similar solutions. It was also found that this effect, which was originally observed with solutions of HCl and HBr, could also be produced by treatment with dilute hydrofluoric acid which is known to attack glass by direct dissolution of the silica network. These observations

suggest that all these halogen acids dissolve the network of soda glass electrodes to a certain extent thus reducing the thickness of the gel layer. The recovery of the electrodes' normal response would then be explained simply as a reconditioning of the surface.

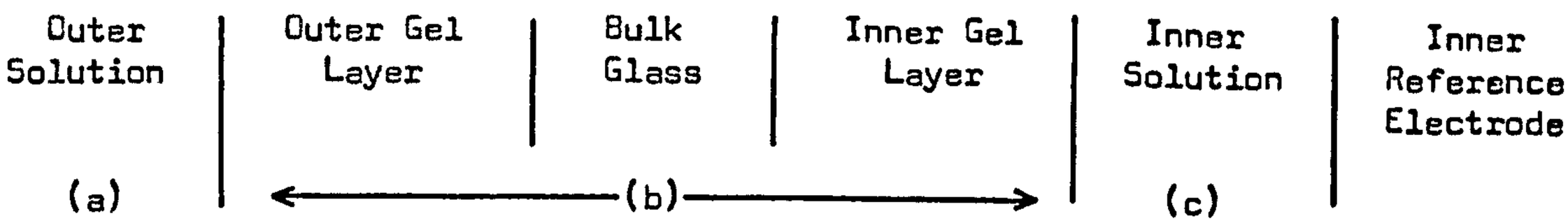
12.2. The Phase Boundary Potential Theory.

The phase boundary potential theory is based upon the experimental evidence, reviewed in the last section, concerning the structure of the membrane of a glass electrode. This membrane is regarded as consisting of three distinct regions, namely, two gel layers on the inner and outer surfaces, and unchanged glass in the centre. The potential across the membrane is regarded as being established at the two gel layer-solution interfaces. Hence the potential of the whole glass electrode is the sum of three contributions, one from each of the two gel layer-solution interfaces, and one from the inner reference electrode. On this basis it is possible to derive an equation which accounts for the main features of glass electrode performance, namely a response of $2.303\frac{RT}{F}$ per pH unit with the possibility of positive errors in alkaline solutions and negative errors in the acid region.

Previous attempts at quantitative developments of the theory have been unrealistic in that they did not take account of all three contributions to the potential, and in some cases they involved unjustified assumptions.

For example, Nikolsky[29] only considered the potential established at the outer surface of the glass membrane and hence made no attempt to account for the asymmetry potential. Schwabe and Glöckner[21] on the other hand assumed that the asymmetry potential is zero when a glass electrode shows the correct pH response, which is not only contrary to experimental fact but, as will be shown later, is also quite unnecessary. The theory will therefore now be reconsidered, taking account of these factors to give expressions for the calibration e.m.f. and the e.m.f's. of other cells used in the present work.

As stated above, the potential of a glass electrode is regarded as the sum of the potentials at the inner and outer surfaces of the glass membrane and the potential of the inner reference electrode. We require the potential across the arrangement illustrated below with the inner reference electrode positive relative to the outer solution



At equilibrium the electrochemical potentials of hydrogen ions in the solution and in the gel layer will be equal both at the inner and outer surfaces of the glass membrane.

$$\text{i.e.} \quad \bar{\mu}_{gi} = \bar{\mu}_i \quad \text{and} \quad \bar{\mu}_{go} = \bar{\mu}_o$$

where the subscript g refers to the glass surface and subscripts o and i refer

to the outside and inside of the glass bulb respectively. The equations may be rewritten in terms of the chemical potential of the hydrogen ions and the potential ψ of each phase

$$\mu_{gi} + F\psi_b = \mu_i + F\psi_c \quad \text{and} \quad \mu_{go} + F\psi_b = \mu_o + F\psi_a$$

$$F(\psi_c - \psi_b) = \mu_{gi} - \mu_i \quad \text{and} \quad F(\psi_b - \psi_a) = \mu_o - \mu_{go}$$

Hence the potential across the whole glass electrode is given by:-

$$E = E_{ref} + (\psi_c - \psi_b) + (\psi_b - \psi_a)$$

where E_{ref} is the potential at the inner reference electrode.

$$E = E_{ref} + \frac{\mu_{gi} - \mu_i}{F} + \frac{\mu_o - \mu_{go}}{F}$$

Introducing activities instead of chemical potentials for the hydrogen ions one obtains

$$E = E_{ref} + \frac{RT}{F} \ln \frac{a_o}{a_i} + \frac{RT}{F} \ln \frac{a_{gi}}{a_{go}}$$

for the glass electrode potential since the standard chemical potentials for the hydrogen ion in the two solutions and the two gel layers are equal and will cancel out

$$\text{i.e.} \quad \mu^o_i = \mu_o{}^o \quad \text{and} \quad \mu^o_{gi} = \mu^o_{go}$$

The subscripts all have the same meaning as before.

The first two terms on the right hand side of the above equation represent

the ideal hydrogen-ion function of the glass electrode, and if the two solutions are standard solutions for the electrode in question then the third term is the asymmetry potential defined as the e.m.f. of a cell such as 6 in section 5.1 (page 65). Thus the asymmetry potential is given by

$$E_6 = \frac{RT}{F} \ln \frac{a^*_{gi}}{a^*_{go}}$$

where a^*_{gi} and a^*_{go} are the hydrogen ion activities in the two gel layers when they are in contact with standard solutions. The calibration e.m.f. of the electrode defined in section 5.1. as the e.m.f. of cell 7 (page 68):-

(Pt) H_2 (p) | Standard Solution | Glass electrode

is thus given by:-

$$E_7 = E_{ref} + \frac{RT}{F} \ln \frac{a^*_{gi}}{a^*_{go}} - \frac{RT}{F} \ln a_i$$

provided the partial pressure of hydrogen is 1 atmosphere.

An error of the glass electrode is thought to be due to a change in the activity of the hydrogen ions in the outer gel layer and in this sense could be regarded as a change of asymmetry potential. In alkaline solutions the hydrogen ion activity in the outer gel layer will decrease relative to its value when the electrode is placed in a standard solution, causing a positive error, whereas in acid solutions the reverse will occur. A change in the hydrogen ion activity in the inner gel layer may be occurring simultaneously

even though the inner solution remains unchanged, and the changes at the two surfaces are in practise inseparable. However, any change at the inner gel layer is likely to be small and hence the hydrogen ion activity in the inner gel layer is regarded as remaining unchanged when the electrode shows an error.

The potential of a glass electrode when it shows an error is thus given by

$$E = E_{ref} + \frac{RT}{F} \ln \frac{a_{gi}^*}{a_{go}} + \frac{RT}{F} \ln \frac{a_o}{a_i}$$

and this may also be expressed in terms of the calibration e.m.f. as

$$E = E_7 + \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}} + RT \ln a_o$$

The glass electrode error is determined by measuring the e.m.f. (E_3) of the cell:

$$(Pt)\ H_2\ (p) \ \Big|\ \text{Test Solution} \ \Big|\ \text{Glass Electrode}$$

(section 5.1; Cell 3) and if the partial pressure of hydrogen p is one atmosphere, the e.m.f. is given by

$$E_3 = E_7 + \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}}$$

The error of the glass electrode is thus

$$\Delta E = E_3 - E_7 = \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}}$$

As will be seen in section 12.3, Schwabe and Glockner[21] used this form of the

theory when considering the time dependence of the acid errors shown by their soda glass electrodes.

According to the phase boundary potential theory of the glass electrode, the alkaline errors are considered to be due to a reduction in the hydrogen ion activity in the outer gel layer. Nikolsky[29] suggested that this was brought about by an ion exchange process in which hydrogen ions originally present in the gel layer are replaced by cations from the solution. This process proceeds until equilibrium is attained ,

$$H^+_{(g)} + M^+_{(s)} \rightleftharpoons H^+_{(s)} + M^+_{(g)}$$

where M^+ represents a metal cation and the subscripts g and s refer to the glass and solution respectively. The equilibrium constant is given by

$$K = \frac{a_H \; a'_M}{a_M \; a'_H}$$

where the primes indicate that the activities refer to the glass phase. It is assumed that in the glass phase the activities of the ions are equal to their concentrations (i.e. $a'_M = C_M$ and $a_H' = C_H$). Also the number of sites in the gel layer at which ion exchange may occur is regarded as fixed and hence the total concentration of hydrogen and other cations C is constant. Hence

$$C_M = C - C_H$$

and $$C_H \; a_M \; K = a_H \; (\; C - C_H \;)$$

The electrode potential was given earlier as

$$E = E_7 + \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}} + \frac{RT}{F} \ln a_o$$

When the glass electrode shows no error, all the sites in the gel layer are occupied by hydrogen ions and $a_{go}^* = C$. Hence:

$$\frac{a_{go}^*}{a_{go}} \times a_o = \frac{C}{C_H} \times a_H$$

From above $$C_H (a_H + a_M K) = C a_H$$

$$\therefore \frac{C a_H}{C_H} = a_H + a_M K$$

Hence the equation for the electrode potential becomes

$$E = E_7 + \frac{RT}{F} \ln (a_H + a_M K)$$

If the sodium ion activity in solution is much less than that of the hydrogen ion then the electrode shows the correct pH response, if the converse holds, a response to sodium ions is shown. From e.m.f. measurements with an electrode in these two regions, the value of the empirical equilibrium constant K can be estimated for that particular electrode glass. However substitution of this value of K in the equation is often found to show poor agreement with experimental data in the transition region.

This lack of agreement is in all probability due to the fact that the

derivation given above represents an oversimplified picture of the nature of a glass electrode surface. In the first place it is assumed that the gel layer is completely homogeneous and that all cation sites are identical. Also it is assumed that the activities of the cations in the gel layer are equal to their concentrations, or in other words that their activity coefficients are independent of concentration. In an attempt to obtain improved agreement with experimental data, Nikolsky has modified the theory taking account of the first of these factors whereas Lengyel, Csakvari and Boksay[90] have considered the second possibility. However, both these more sophisticated approaches simply result in more elaborate equations with other empirical constants in addition to the equilibrium constant.

Various authors have attempted to extend the phase boundary potential theory by addition of potentials set up by diffusion of cations through the glass. There appears to be some lack of clarity[91] as to whether these diffusion potentials refer to diffusion of cations between the gel layer and the solution or between the bulk glass and the gel layer. However, both these possibilities are inconsistent with the phase boundary potential theory, since the phase boundary potential theory assumes that equilibrium has been established between the solution and the gel layer. Even if the diffusion process is intended to refer to the movement of hydrogen ions from the gel layer into the bulk glass to replace the cations originally present, the cations from the bulk glass which diffuse into the gel layer must finally pass into the solution, if the gel layer is to remain at constant composition.

Hence while the phase boundary potential theory as derived above is an oversimplified view of the glass electrode, modification of the theory by combination with diffusion potentials is not satisfactory on account of the incompatibility of the models used in the two approaches.

12.3. Theories of the Time-Dependence of Glass Electrode Potentials.

When devising theoretical equations for the time dependence of glass electrode potentials it must be remembered that at least two distinct situations may arise. First one has the case of an electrode primarily responsive to a given cation, placed in a solution where it shows a time dependent error in that response, for example the acid and alkaline errors of pH responsive electrodes. Second one may be concerned with the speed of response of an electrode to a rapid change in the activity of a single potential determining cation in solution. It is important when comparing a theoretical equation with experimental data to ensure that the conditions pertaining in the experiment correspond essentially to those assumed in the theory.

The first possibility has been examined by Schwabe and Glockner[21] for the case of the acid errors of soda glass electrodes. The second possibility has been considered by Rechnitz and Hameka[92] and Johansson and Norberg[93] and both these groups arrived at an equation giving the logarithm of potential as a linear function of time. The equation of Schwabe and Glockner in which

the acid error is expressed as a function of the logarithm of the time is the mathematical converse of this. Muller[94] has recently suggested a Langmuir Isotherm type of equation namely:

$$E = \frac{t}{a + bt} \qquad \text{or} \qquad \frac{t}{E} = a + bt$$

where E is the potential difference after time t and a and b are empirical constants, for the case of an electrode response to change in the activity of a single cation in solution. This equation does not appear to have been tested against experimental data although Muller claims that it fits the time variation of the potential across an Orion silver sulphide membrane electrode, resulting from a change in silver ion activity in the adjacent solution. Caudle[1] attempted to fit this type of equation to the different situation of the acid errors of his soda glass electrodes but discarded it as too insensitive. He found that the parameters a and b were not constant for any particular electrode or any particular solution and therefore concluded that they were of no use as an aid to the interpretation of glass electrode response.

Schwabe and Glockner attempted to obtain theoretical justification of the time dependence of the acid errors shown by their MacInnes-Dole glass electrodes on the basis of the phase boundary potential theory. They claimed that for certain acid solutions, the time dependence of the errors corresponded to the empirical equation

$$-\Delta E = A + B \log (C + t)$$

where t is the time after first placing the electrode in the acid solution

and A, B and C are constants. However as will now be shown, neither the equation nor the explanation advanced by Schwabe and Glockner are consistent with many of the results obtained in the present work.

Schwabe and Glockner assumed that the error was always zero at t = 0 and hence

$$A = -B \log C$$

$$\text{and:-} \quad -\Delta E = B \log \frac{C + t}{C}$$

$$\text{or:-} \quad \text{antilog} \frac{-\Delta E}{B} = 1 + \frac{t}{C}$$

However the first two of these equations are mathematically unsatisfactory as they involve the logarithm of a quantity which has units, namely time. It would be better to replace A by a constant m, having the units of time^{-1}, such that

$$-\Delta E = B \log m (C + t)$$

$$(A = B \log m)$$

This equation may be rearranged to give

$$q = \text{antilog} \frac{-\Delta E}{B} = mC + mt$$

and is not only mathematically correct, but is also more general in that it does not require $\Delta E = 0$ when $t = 0$. A graph of q against t should be linear with slope m and intercept mC. If the error is zero when $t = 0$, then the intercept will be unity.

It was stated earlier that according to the phase boundary potential

theory of the glass electrode, the acid error is thought to be due to the hydrogen ion activity in the outer gel layer increasing over the value pertaining when the electrode is placed in a standard solution. Where their equation was obeyed Schwabe and Glockner considered this increase to be due to excess hydrogen ions entering the gel layer from the solution. Electroneutrality of the glass would be maintained by a corresponding uptake of anions. Where the equation did not hold they suggested that the increase in hydrogen ion activity in the outer gel layer was due to dehydration of the layer by the concentrated acid solution.

Schwabe and Glockner suggested that their empirical equation was consistent with the phase boundary potential theory, if the activity of hydrogen ions in the outer surface of the glass, increases linearly with time when the electrode is placed in the acid solution. As was seen in the last section, according to the theory the error of a glass electrode is given by

$$\Delta E = \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}}$$

and hence if the increase in a_{go} after time t is x then $a_{go} = a_{go}^* + x$ and the error is given by

$$\Delta E = \frac{RT}{F} \ln \frac{a_{go}^*}{a_{go}^* + x}$$

If x is a linear function of time, i.e. $x = kt$, then

$$-\frac{\Delta E}{59.16} = \log \frac{a_{go}^* + kt}{a_{go}^*}$$

which corresponds to the empirical equation if B = 59.16mV, mC = 1 and

$$m = \frac{k}{a_{go}^*} \quad time^{-1}.$$

Schwabe and Glockner make the unrealistic assumption that the asymmetry potential of a glass electrode is zero when there is no error, in order to achieve essentially the same result. Their assumption involves putting $a_{gi}^* = a_{go}^*$ and hence they obtain

$$\text{antilog } \frac{-\Delta E}{59.16} = 1 + \frac{kt}{a_{gi}^*}$$

However, as has been shown, the assumption is entirely unnecessary since the same result may be achieved without it.

Schwabe and Glockner tested their electrodes for periods of up to 30 hours in HCl, H_2SO_4 and H_3PO_4 at various concentrations. They then plotted values of $q = \text{antilog } \frac{-\Delta E}{59.16}$ against time, and if their interpretation was correct, these graphs would be linear with unit intercept. In some cases a linear relationship between q and t was observed but in others the slope of the curve decreased with increase in t and the error, and hence q, tended towards a constant final value. In HCl this change of slope was not apparent even after 30 hours whereas in H_2SO_4 and H_3PO_4 it took place after a few hours, depending upon the experimental conditions such as the acid concentration; Only in 5M and 4M HCl was the error not zero when t = 0. However the potential changed very rapidly immediately after the electrode was placed in one of these solutions and it is possible that a much smaller error would have been observed if the first measurement had been made a little earlier. Schwabe and

Glockner point out that this was also true of the data obtained by Sinclair and Martell[19] for a MacInnes-Dole electrode in 5M HCl although it is not clear exactly what time Sinclair and Martell transferred their electrode to this solution. (See Table 12.1. - Sinclair and Martell apparently transferred their electrode to 5M HCl at some time between 7.25 pm and 7.55 pm.)

Comparison of the data of Schwabe and Glockner for 5M HCl with their q-t graph suggests that for this solution they plotted $q = \text{antilog} -\left(\frac{\Delta E - \Delta E_o}{59.16}\right)$ against t, where ΔE_o is the error when $t = 0$. (ΔE_o is the first observed error rather than the "instantaneous error" obtained by extrapolation of the e.m.f.-time curve.) This plot is linear and would be consistent with the empirical equation:-

$$-\Delta E = B \log m (C + t)$$

since then: $$-\Delta E_o = B \log mC$$

and hence: $$-\left(\frac{\Delta E - \Delta E_o}{B}\right) = \log \frac{C + t}{C}$$

However it would be inconsistent with their theoretical explanation which requires $\Delta E_o = 0$ and $m = \frac{1}{C}$. Table 12.1. corresponds to Schwabe and Glockner's "table 1", which is the only table in their paper that gives the actual values of the errors shown by one of their electrodes. All their other data are only presented graphically. As can be seen, this table includes some of the data of Sinclair and Martell, and although it is not clearly stated it seems fairly certain from comparison with Sinclair and Martell's original paper, that all the data in this table refer to 5M HCl at 25°C. Values of

TABLE 12.1.

Schwabe and Glockner Table 1.

Errors of MacInnes-Dole Glass Electrodes - probably in 5M HCl

Sinclair + Martell			Schwabe + Glockner	
Time 7.25 pm	1M HCl 5M HCl Error (mV)	Time (min) as given by Schwabe + Glockner	t(min)	ΔE (mV)
7.55 pm	-33.1	0	0	-41.0
8.45 pm	-50.4	50	60	-55.1
9.30 pm	-58.5	95	120	-63.5
10.15 pm	-63.8	140	720	-99.1
10.05 am	-100.6	850		
10.30 am	-101.2	875		
11.0 am	-101.8	905		
11.55 am	-118.0	960	1080	-110.5

TABLE 12.2.

Data for Figure 32 (based on Schwabe and Glockner)

Time (hours)	Error (mV)	Antilog $\frac{-\Delta E}{59.16}$	$\Delta E - \Delta E_o$ (mV)	Antilog $-\left(\frac{\Delta E - \Delta E_o}{59.16}\right)$
0	-41.0	4.9	0.0	1.0
1	-55.1	8.5	-14.1	1.7
2	-63.5	11.2	-22.5	2.4
12	-99.1	46.8	-58.1	9.5
18	-110.5	74.1	-69.5	14.8

antilog $\frac{-\Delta E}{59.16}$ and antilog $-\left(\frac{\Delta E - \Delta E_o}{59.16}\right)$ have been calculated from this data of Schwabe and Glockner and are given in table 12.2. q = antilog $-\frac{\Delta E}{59.16}$ is plotted against time in figure 32a and the corresponding plot (figure 3) from Schwabe and Glockner's paper is reproduced in figure 32b.

It can be seen that the two graphs are not the same and that the points for 5M HCl in figure 32b appear to fit the values of antilog $-\left(\frac{\Delta E - \Delta E_o}{59.16}\right)$. However the graph of antilog $\frac{-\Delta E}{59.16}$ against time is linear and considering the uncertainty in the exact time when the electrode was placed in the solution, the intercept is approximately one. Schwabe and Glockner comment on the fact that the slopes of the q-t curves increase with acid concentration and the values of $\frac{dq}{dt}$ are tabulated. The units are not stated but from figure 32b appear to be in hours^{-1}.

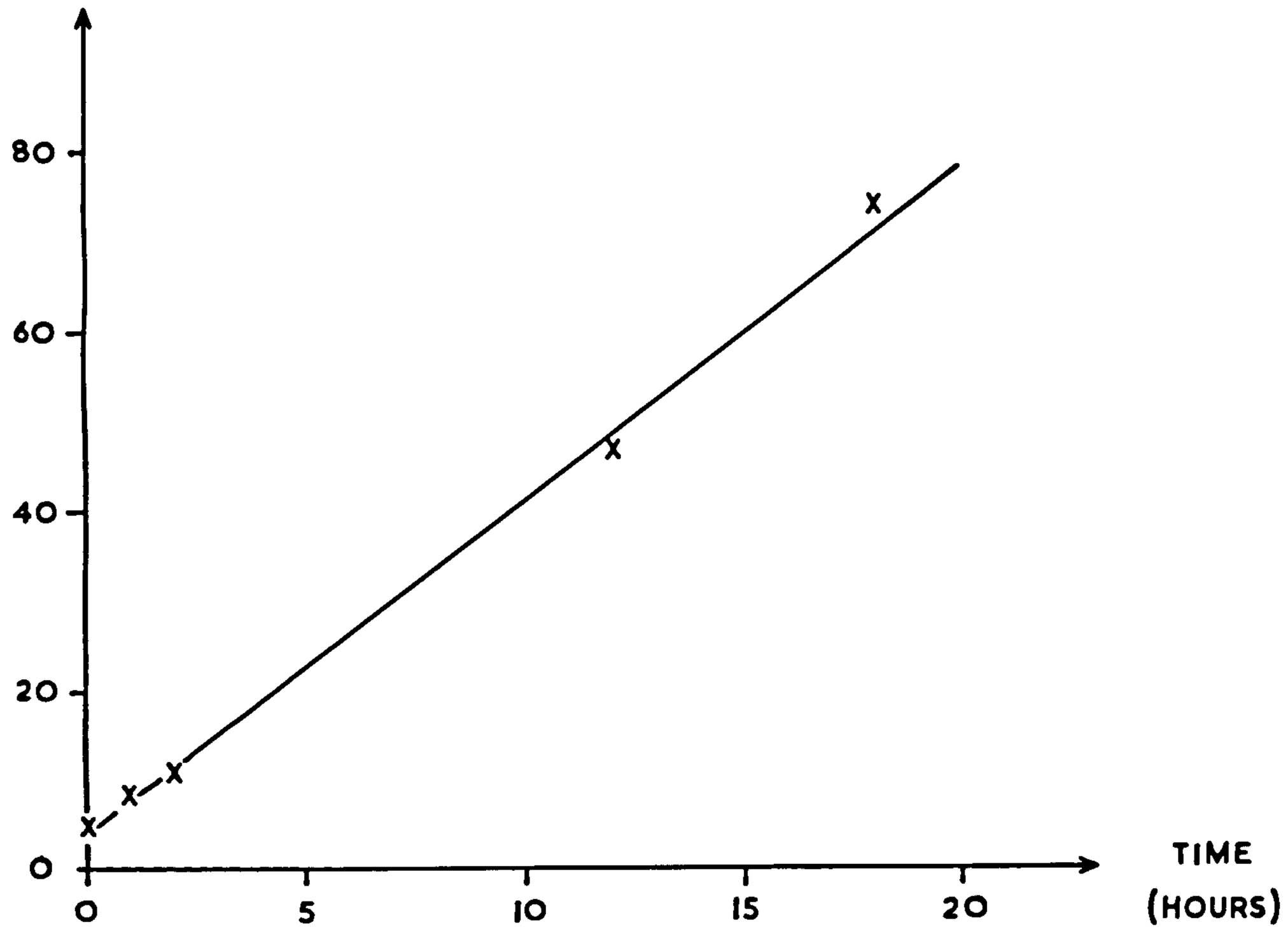
Schwabe and Glockner - Table 2

HCl Concentration	3M	4M	5M
$\frac{dq}{dt}$ (hours^{-1})	0.19	0.47	0.76

The slope of the plot in figure 32a is however approximately 4 hours^{-1}.

If their graph for 5M HCl represents a different experiment to that given in the table, it would appear that the slope of the q-t curve and the magnitudes of the errors for a given solution are partly dependent upon some other variable such as the age of the electrode but no mention is made of this. However, they stated that $\frac{dq}{dt}$ was dependent upon the time for which the electrode had been conditioned but implied that they had eliminated this

a) This Work.



b) Original Paper.

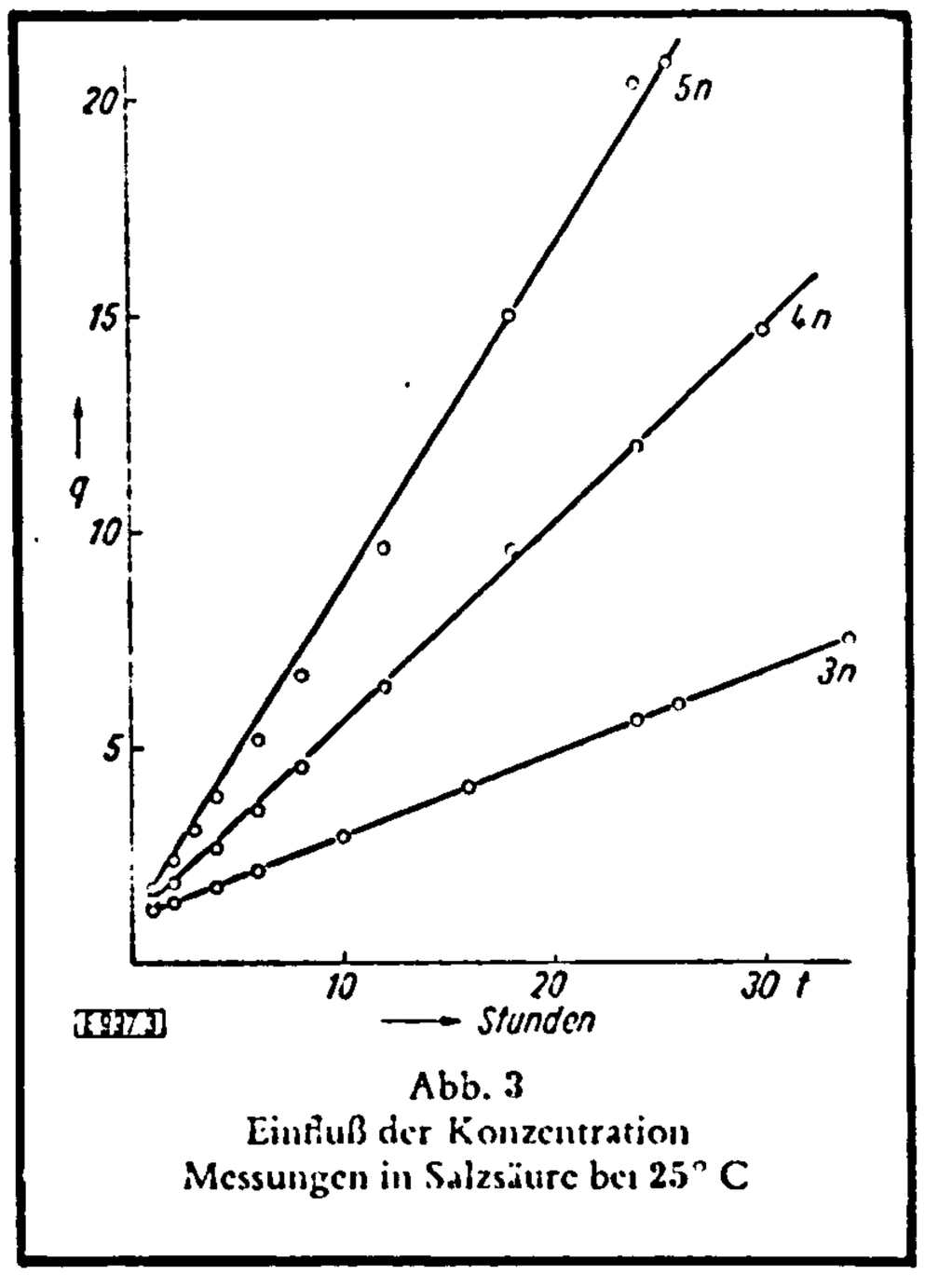


Abb. 3
Einfluß der Konzentration
Messungen in Salzsäure bei 25° C

Fig. 32 DATA OF SCHWABE & GLÖCKNER Error in 5M HCl at 25 °C

variable by soaking all their electrodes in distilled water for at least 14 days. On the other hand, if the tabulated data refer to a different temperature it seems inappropriate to compare them with the data of Sinclair and Martell for 25°C.

A large number of the e.m.f.-time curves obtained in the present work cannot be explained by the theory of Schwabe and Glockner which involves the following two assumptions.

1. The activity of hydrogen ions in the outer gel layer does not change discontinuously. i.e. $a_{go} = a_{go}^{*}$ at $t = 0$ in a concentrated acid solution and hence $\Delta E = 0$ when $t = 0$.
2. The change in a_{go} in an acid solution is a linear function of time. This means that the error cannot show turning points.

In this work, the e.m.f.-time curves in which the error was initially decreasing rapidly have frequently been observed both for acid and alkaline solutions. Extrapolation of such a curve cannot possibly give zero instantaneous error. These transients can only be consistent with the first of the assumptions above if it is postulated that the error showed a rapid increase during the time between transfer of the electrode and switching on the measuring circuit. However, this would not satisfy the second assumption, and for the same reason any transient where a turning point was observed is inconsistent with Schwabe and Glockner's theory. Hence the theory cannot account for transients of types D_1, D_2 and C_2 and this only leaves type C_1 of which comparatively few examples have been observed.

Rechnitz and Hameka[92] have derived an equation for the time variation of the potential shown by a glass electrode after a sudden change in the concentration of the only potential-determining cation in the solution. From consideration of the movement of these ions across the glass-solution interface, they obtained the equation

$$\log \frac{E_{\infty} - E_t}{E_{\infty}} = \frac{-\gamma t}{2.303}$$

where E_t is the glass electrode potential at a time t after the change in solution, E_{∞} is the potential when equilibrium has been attained and γ is a constant dependent upon the nature of both the electrode glass and the potential-determining ion. Rechnitz and Hameka applied the equation to some data obtained by Savage and Isard[47,48] for three rather sluggish electrodes of different glass compositions in experiments with solutions containing potassium ions. They found that graphs of the left hand side of the above equation against time for the various experiments were linear as predicted by the theory.

However, as was noted in section 11.3, it is quite possible in view of the observations of the present work, that the sluggishness observed by Savage and Isard was due to their electrodes showing a mixed response involving the hydrogen ion and was not characteristic of response to a single alkali metal cation. Hence any agreement between the data of Savage and Isard and the equation of Rechnitz and Hameka should probably be regarded as purely fortuitous and not evidence in support of the theory.

Although Rechnitz tested his theory using data of Savage and Isard, he had himself investigated the speed of response of cation selective glass electrodes.[95] He tested a Beckman electrode in both sodium and potassium solutions and in contrast to Savage and Isard concluded that the electrode potential reached within ±0.5mV of its final steady value in a few seconds. However Rechnitz conditioned the electrode by soaking it for 24 hours in a solution of the appropriate salt and all the solutions employed were relatively concentrated (0.05 - 1.0M). It is of course possible that cation selective electrodes made from certain glass compositions are sluggish in their response to change in the concentration of a single cation and that Savage and Isard's electrodes were examples of this. However, before such data can be regarded as supporting the theory of Rechnitz and Hameka, it is necessary to establish that they are not the result of a mixed electrode function.

It is not clear from their paper[48], whether Savage and Isard themselves consider the time dependence of the potentials of their electrodes to be due to a sluggish response to a single ion or a mixed response. For the case of a mixed response, they suggest that the ion exchange sites on the surface of the gel layer have different properties to those in the bulk of the layer. After a sudden change in the solution, the surface sites would attain equilibrium more rapidly than the others and temporarily influence the electrode potential.

Johansson and Norberg[93] investigated the speed of response of pH

sensitive glass electrodes with an experimental procedure which involved changing the solution around an electrode rather than moving the electrode itself. They also used the theory of electrochemical kinetics to devise an equation for the time dependence of a glass electrode potential when subjected to a change in the activity of a single cation in solution. The equation is limited to 10-fold changes of cation activity and Johansson and Norberg claimed that the equation fitted their experimental data for glass electrodes subjected to changes of pH in non-aqueous solvents. The electrode response was much faster in aqueous than in non-aqueous solutions and hence for experiments with aqueous solutions a method of producing a very fast pH change was devised using syringes. Nevertheless it was found that the rate of response was independent of pH over a wide range and by repeating the experiment with silver nitrate solutions and a silver electrode, which is known to have a fast response, it was shown that the speed of response of their glass electrodes in aqueous solutions, was limited by the time taken to replace one solution by another.

Johansson, in collaboration with Wikby[96], has also attempted to obtain information concerning the mode of operation of glass electrodes by investigation of their resistances measured both with a.c. and d.c. These workers subjected their electrodes to a current pulse and suggested that the subsequent variation of potential could be resolved into contributions from four main sources each with a different time constant. Each time constant could be represented by an equivalent circuit with a resistance in

parallel with a condenser. Two of these processes were fast with time constants measured in msec., whereas the other two were slower with time constants of the order of tens of seconds. They claimed that the fast processes originated in the bulk of the glass rather than at the surface and could be related to the thickness of the membrane. The activation energies of the resistances in the equivalent circuits were also equal to the values for the d.c. resistance of the bulk glass. The slow processes on the other hand were believed to originate at the glass surface since their time constants and the resistances in the equivalent circuits depended upon the hydration of the glass.

At the beginning of this section, attention was drawn to the importance of ensuring that, when a theory of the glass electrode is tested against experimental data, the situation envisaged in the theory actually applies to the experimental conditions. There are two distinct situations, a response to a single cation or a mixed response.

The response of a glass electrode to a change in the activity of a single potential-determining cation in solution has been shown to be very rapid, both for pH responsive electrodes and those responsive to alkali metal ions. In fact the time taken after transfer, for an electrode to attain a steady potential, was often less than the time required to obtain the first e.m.f. reading. With some electrodes small changes of potential were observed over the first few minutes, which were thought to be electrical in origin (feature A), but even in the absence of these the

response time was too fast to be observed with the experimental technique used here. This technique involving transfer of the glass electrode, was chosen because it approximates most nearly to the procedure used in practice when making pH, pNa or pK measurements with glass electrodes. Hence in order to investigate the time dependence of the response of an electrode to change in the activity of a single potential-determining ion in solution, it is necessary to use an experimental technique which involves changing the solution around the electrode rather than moving the electrode itself[1,93].

For the case of an electrode showing an error in its normal response to a particular cation, it has been found in the present work that a wide variety of e.m.f.-time variations is possible. Attempts to fit a selection of these to the various equations mentioned at the beginning of this section, were without any real success. In fact the situation is undoubtedly more complex than envisaged in the theories presented by previous authors, from which some of these equations originate. Hence although qualitative explanations for some of the observations of the present work were suggested in section 12.1, the present state of knowledge is such that no useful purpose would be served by any quantitative discussion.

Conclusions.

The main conclusions of this investigation concerning the response characteristics of glass electrodes may be summarised as follows.

1. Using a suitable experimental technique the best pH responsive glass electrodes agree with the hydrogen electrode to ±0.2mV., and often better, when transferred between solutions of widely differing pH.

2. The errors shown by lithia glass electrodes in alkaline solutions containing lithium ions are larger than those observed for sodium solutions of the same pH and cation concentration.

3. Lithia glass electrodes have been shown to be error-free within ±0.2mV at pH 13 in a solution of tetraethylammonium hydroxide in which the sodium ion concentration was very small. It has also been shown that soda glass electrodes agree with the hydrogen electrode to ±0.2mV or better up to p_wH 10.5 when transferred to solutions buffered with tris or ethanolamine which do not contain small inorganic cations. These results demonstrate that the alkaline errors of glass electrodes are not caused by the high pH alone but the solution must also contain a significant concentration of one or more of the small inorganic cations.

There is evidence from radioactive tracer work that the small inorganic

cations are responsible for the alkaline errors and are adsorbed on to the glass surface at high pH. The fact that errors are not observed in the absence of these ions provides further support for this view.

4. It has been shown, using soda glass electrodes, that under certain circumstances, previous treatment has an influence on the response. This possibility had been suggested before but no definite experimental evidence had previously been obtained. It has been found that treatment of a soda glass electrode with an HF, HCl or HBr solution in which it shows an error causes a change in its response in alkaline solutions.

There is also evidence from the results of this investigation that electrodes are uninfluenced by the nature of any standard solutions in which they are placed, except of course the pH. The response of the electrodes in alkaline solutions was apparently independent of the nature or pH of the standard solution from which they were transferred. The recovery of a soda glass electrode from the effect of treatment with HCl was not particularly fast when it was standing in 1.0m H_2SO_4. Hence the sulphuric acid does not appear to have the special conditioning effect suggested by Caudle[1], and probably one standard solution is as good as another.

5. The acid errors of soda glass electrodes are much less reproducible than the errors in alkaline solutions.

6. When glass electrodes were tested in concentrated magnesium sulphate solutions they agreed with the hydrogen electrode within the precision of the experimental method and did not show a "water activity error" as has previously been reported.

7. Under suitable experimental conditions the response of cation sensitive electrodes is as rapid as that observed for the best pH responsive glass electrodes.

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